FINAL PROJECT REPORT

DISTRIBUTION OF CONTAMINANTS IN WATERS OF MONROE HARBOR (RIVER RAISIN), MICHIGAN AND ADJACENT LAKE ERIE

by

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ABSTRACT

Monroe Harbor, Michigan, at the confluence of the River Raisin and western Lake Erie, has been identified by the International Joint Commission as a "Class A Area of Concern". Previous state and federal studies of the site have documented water quality problems that included contamination of water, sediments and fish with certain organic and metal toxins. The current project was designed to address questions of contaminant distribution, fate and biological effects in this aquatic system. This data report describes the results of surveys of selected organochlorines and metals in waters of Monroe Harbor and adjacent Lake Erie.

Contaminants emphasized in the study were polychlorinated biphenyls (PCBs) and heavy metals (chromium, copper, zinc) which were known to be prevalent in the system, and were potentially toxic at current levels. Seasonal surveys of contaminant distribution in the water column were designed to support exposure/effects studies and mass balance modeling. For descriptive purposes, the concentration data were plotted as spatial profiles (i.e., by station) for all surveys, and as temporal profiles (i.e., by survey) for selected stations. Both total and particulate PCBs and total and filtrate (i.e., "dissolved") metals were measured in composite and/or grab samples.

The distribution data for three representative sites sampled in all 10 surveys indicate the following. Mean concentration values at Station 1

represented the upstream boundary conditions of 8.6 ± 3.0 ng/L for total PCBs, 2.3 ± 1.9 μg/L for total chromium, 4.1 ± 2.1 μg/L for total copper, and 8.3 ± 5.8 μg/L for total zinc. Downriver near the turning basin (Station 4), concentrations generally increased to 119 ± 121 ng/L for total PCBs, 3.1 ± 1.9 μg/L for total chromium, 4.7 ± 2.3 μg/L for total copper, and 8.5 ± 4.8 μg/L for total zinc. Further downriver at or near the river mouth on Lake Erie (Stations 6 or 26), concentrations generally decreased to intermediate levels of 18 ± 10 ng/L for total PCBs, 2.6 ± 1.7 μg/L for total chromium, 4.3 ± 2.2 μg/L for total copper, and 10 ± 5.8 μg/L for total zinc. Relative to both the upriver and lake boundary conditions, PCB concentrations in the turning basin were dramatically higher. Metals concentrations tended toward slightly higher levels in the turning basin and the lake relative to the upriver boundary levels. In general, the contaminant concentrations in water were highest at the power plant discharge near Lake Erie (Station 29). Concentrations of all four contaminants were more variable but not markedly higher during high flow conditions in the spring.

Potential sources of contaminants that may elevate concentrations at or below the turning basin include the Monroe WWTP (mainly zinc and PCB), automotive and paper plant discharges (PCB), and polluted turning basin sediments (metals and PCB).

Where both surface and bottom waters were sampled below the turning basin, PCB concentrations were higher near the surface, and metal levels were more elevated near the bottom.

Some technical problems concerning PCB sample clean-up and routine collection of filtrate and particulate fractions for PCB analysis were not fully resolved in this study.

Additional water quality data, which may relate to toxicity effects or contaminant availability, was not presented here, but will be included in forthcoming reports on modeling results.

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ABBREVIATIONS AND SYMBOLS

AAS	- Atomic Absorption Spectroscopy
CFS	- Cubic Feet Per Second
DCM	- Dichloromethane
ECD	- Electron Capture Detector
EMSL	- Environmental Monitoring and Support Laboratory
EPA	- Environmental Protection Agency
i.d.	- Inner Diameter
IJC	- International Joint Commission
KD	- Kuderna-Danish
LAS	- Laboratory Automation System
LLRS	- Large Lakes Research Station
LPE	- Linear Polyethylene
MDNR	- Michigan Department of Natural Resources
MGD	- Million Gallons Per Day
NOAA	- National Oceanographic and Atmospheric Administration
PCB	- Polychlorinated Biphenyl(s)
PSI	- Pounds Per Square Inch
PVC	- Polyvinyl Chloride
QC	- Quality Control
USEPA	- United States Environmental Protection Agency
USGS	- United States Geological Survey
WWTP	- Waste Water Treatment Plant

Cr	- Chromium
Cu	- Copper
HNO_3	- Nitric Acid
H_2SO_4	- Sulfuric Acid
N_2	- Nitrogen
Ni	- Nickel
Zn	- Zinc

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1.0 INTRODUCTION

The mouth of the River Raisin on western Lake Erie has been designated by the International Joint Commission (IJC) as one of 42 "Class A Areas of Concern" in the Great Lakes system. This portion of the River Raisin, which is partially dredged for navigation, has been one of the most severely polluted areas due to the local concentration of industries, landfills and discharge of the wastewater treatment facilities. Even though significant improvements in water quality have been made in the past decade, residual concentrations of toxic substances have remained in the water, sediments and biota.

Because of its history of contamination problems, this site was selected in 1983 by the EPA Large Lakes Research Station for a prototype study to develop field methodologies and protocols for assessing ecological effects of toxic substances. The primary purpose of the study has been to develop a predictive capability whereby effects of substances could be estimated, given their source loadings, transport and fate characteristics. To date, ten separate research organizations have been involved with the project, which has required focused, coordinated efforts by all.

This report presents only that part of the project which dealt with defining the gradients of toxic substances within the water column. All of the data have been stored in a computer data base and are available to all

investigators for further assessment and correlation of chemistry with effects.

Secondarily, these data will provide an update on the status of water quality for regulatory agencies, and may provide information which could lead to mitigative actions. The data also will be used to calibrate a mass balance model which may be useful in the regulatory process. Most importantly, the study has led to development of research methods for dealing with toxic substances in other highly impacted areas of the Great Lakes.

1.1 CONCLUSIONS

The following conclusions were reached as a result of this study of contaminant distribution in Monroe Harbor and adjacent Lake Erie waters.

(a) A large data base was compiled on the spatial and temporal distribution of chromium, copper, zinc, polychlorinated biphenyls (PCBs) and other selected organochlorines in the water column of this contaminated harbor system. Measurements were made on both whole (unfiltered) water and filtrate or particulate fractions of water throughout the lower River Raisin and its discharge into Lake Erie. The data will permit calculations of partition coefficients for these contaminants.

(b) In addition to the total PCB results described in this report, the study also provided quantitative results for individual PCB congeners and homologs. This analysis was based on high-resolution gas chromatography using the first complete set of synthetic PCB standards. The results showed the feasibility of applying congeners-specific PCB analysis to a large number of environmental samples representing water and other media.

(c) The resulting spatial profiles of PCBs and metals generally show that concentrations seen at the upstream boundary of Monroe Harbor increased somewhat near the turning basin, and gradually diminished downstream toward the Detroit Edison power plant intake. At that point, concentrations often declined abruptly due to the presence of Lake Erie water drawn upriver by the plant.

(d) The plant discharge southward near the mouth of Plum Creek produced its own water quality gradient or plume in Lake Erie. However, this gradient was generally not well-defined by contaminant levels, except by zinc in Survey 4 and by copper in Survey 5.

(e) Levels of PCBs and metals at the upstream boundary (Station 1) and in the open lake (Station 11) were typically similar within an order of magnitude. Seasonal changes in concentrations at both sites were within a factor of 2 or 3.

(f) Periodic high concentrations of PCBs at Stations 8 and 4 near the turning basin indicated continuing sources of these contaminants. A mass balance study in progress will address the sources and fate of this material. It is not clear at present whether the highest levels of PCBs observed in Mason Run (Station 8) were important in terms of PCB mass being loaded to the turning basin.

(g) Temporal profiles indicate that PCB and metal concentrations were most variable under high flow conditions in the spring. However, the mean values during high and low water conditions were not markedly different at the upstream boundary (Station 1). Concentrations of PCB and metals in Monroe Harbor underwent large fluctuations at times, especially within the turning basin. This

may have depended on flow conditions in the river, as well as changes in rates of point source loadings. Contaminated sediments at this site (see Filkins et al., 1985) may have been a major source of pollutants during resuspension events.

(h) Two principal sources of metal loadings were recognized from these surveys. Zinc at concentrations 5 to 10-fold higher than in the river was regularly discharged from the Monroe WWTP (Station 7). In contrast, copper and chromium levels in this effluent were generally lower than in the adjacent river. The second principal source of all three metals was apparently the automotive plant (Ford) effluent at Station 9. There, levels were generally an order of magnitude higher than in upstream river water. However, after dilution at the river outfall (Station 5), the concentrations were reduced to near ambient levels. Whether or not other primary sources of contaminants exist may be indicated by the results of mass balance modeling. For example, an extensive landfill area along the south shore of Monroe Harbor is known to contain toxic wastes (MDNR, 1983) and may be another source of contamination via ground water.

(i) Where surface and bottom water were sampled regularly at Station 4, PCBs concentrations seemed to be consistently higher in surface water. However, metal concentrations were slightly more elevated in bottom water.

(j) Difficulties were encountered in cleaning up dichloromethane extracts of some Monroe Harbor water samples prior to PCB analysis.

As a result, PCB quantitation has not been completed for these samples.

(k) Further analysis of the data will be necessary to compare the results of concurrent grab and composite sampling over 24-hour periods at each station. While daily grab sampling is more economical, composite samples are more likely to reflect pulsed loadings or periodic resuspension of contaminants. For Survey 1 only, the composite values averaged 10% higher than comparable grab values.

(l) Changes in ratios of dissolved (or particulate) fractions to total PCBs and metals, as a function of suspended solids concentrations, may be defined after further analysis of these results. However, difficulties were encountered in making reliable measurements of PCB levels in filtrate and particulate samples. The problems were mainly due to contamination of filters or filter holders, and to insufficient mass collected in smaller volume samples prepared under time constraints in the field.

(m) Analysis of system blanks, filter blanks and Florisil® blanks indicated that method interferences were seldom more than 10% of sample values.

(n) Replicate analysis of Aroclor mixture 1262 showed a consistently high value as compared to the true value. Further investigation is necessary to determine the cause of this bias.

(o) Concentrations of chromium, copper and zinc observed in Monroe Harbor and adjacent Lake Erie were all well below the EPA Water Quality Criteria (1976) values for drinking water. However, copper

and zinc levels in the river were generally within an order of magnitude of those which have produced inhibitory effects in crustacea (Mount and Norberg, 1984).

(p) The quality control measures as applied in the organics work proved to be more useful for documenting the quality of results than for managing the quality of field and laboratory processes in progress. Most of the final PCB data was not available until after all of the field surveys were completed. Metals QC results were generally available within a month after sampling.

(q) While this study was focused on selected toxic metals and organochlorines which were certainly among the major contaminants of the Monroe Harbor system, the possibility remains that other unstudied contaminants were present at concentrations sufficient to cause biological effects. Another study (Mathews et al., 1985) has examined relationships between the selected contaminant levels and various bioassay results. The present report also does not include the results of more conventional analyses for ammonia, chlorine, chloramines, nitrates and other water quality factors which might contribute to toxicity.

1.2 RECOMMENDATIONS

Based on the results and conclusions of the Monroe Harbor study, the following recommendations are made.

(a) Further, intensive studies of this type should address the possible role of in-place contaminants in causing ecosystem effects within other Great Lakes areas of concern. Experience gained at Monroe Harbor will be useful in designing such studies.

(b) There is need to develop more efficient techniques for organic extraction of large-volume water samples to support intensive surveys of this type. Complementary methods are needed also for sampling and processing solute (or filtrate) and particulate fractions of water samples.

(c) The unique distributional data produced here for PCB congeners should be used to study the environmental behavior, chemical fate and biological effects of individual PCBs, especially the more toxic congeners.

(d) Elevated PCB levels observed in the Monroe Harbor turning basin indicate a need for evaluation of sediments and groundwater as possible major sources of contaminants in this system. The source of relatively high zinc levels in the Monroe Wastewater Treatment Plant discharge should be investigated as well.

(e) In other such analytical studies which support biological effects work, more preliminary work should be planned to identify all classes of toxins present at levels which might produce effects in test organisms. Preliminary work also should be focused on suitable methods for sampling and analysis based on chemical matrix problems, if any. Finally, the sampling program design should be founded on more detailed reconnaissance of general water quality indicators.

2.0 BACKGROUND

2.1 BASIN DESCRIPTION

The River Raisin drains an area of 1,070 square miles (2,771 km^2) and discharges into Lake Erie at Monroe, Michigan. A portion of Michigan's southeastern lower peninsula and the northeastern portion of Fulton County, Ohio lie within the boundaries of the basin. The drainage basin narrows down to a 2.5 mile (4 km-wide) strip for the last 15 miles (24 km) of the river (Figure 2.1). The area consists mainly of clay till reworked by glacial lake water and veneered by lacustrine sands, silts, and clays. Two-thirds of Monroe County are covered by a layer of this glacial drift that is less than 50 feet (15 m) in thickness. The underlying bedrock is mostly carbonate in composition (Mozola, 1970).

2.2 HYDROLOGY

Monroe County is essentially flat terrain. There is a gentle slope southeastward from a maximum elevation of 730 feet (223 m) in the northwest corner to 572 feet (174 m) at Lake Erie. This gradual decline of only 158 feet (48 m) in nearly 26 miles (42 km) explains the low velocities of streams located in the county (Mozola, 1970).

Runoff in the drainage basin is significant due to the clay till. The runoff during rain events creates rapid stream fluctuations and very turbid waters. Relative to other areas in Michigan, erosion in the River Raisin

basin is considered to be high. The U.S. Department of Agriculture estimated that 8.3 to 10.8 tonnes of topsoil per hectare per year are lost (Michigan DNR, 1979). A 1967 paper by the U.S. Department of the Interior reported that the average annual precipitation for the drainage basin area is 31.52 inches (80.1 cm). Of this amount, approximately one-third runs off through the river system.

Much of the area adjacent to the River Raisin is prone to flooding. A large portion of the eastern fringe of the city of Monroe was marshland. Over the last thirty years, approximately 80% of the marshlands have been filled in for industrial and recreational uses. The river banks and surrounding areas at the mouth of the River Raisin are man-made (Monroe County Drain Commission, 1984).

The U.S. Geological Survey (USGS) maintains a stream flow gauge (Station #04176500) in the River Raisin near Monroe. It is located in Monroe County, on the left bank of the river (1.3 km downstream from the bridge on the Ida Maybe Road), at latitude 41°57'38" and longitude 83°31'52". The drainage area above this point in the river is 1,042 square miles (2,699 km^2). The average discharge for a record period (1937-1981) was 709 cubic ft/sec (19.9 m^3/sec). The maximum and minimum discharge for the record period was 14,500 cubic ft/sec (407.3 m^3/sec) and 2 cubic ft/sec (0.06 m^3/sec), respectively (USGS, 1982). River flows for an 11-year period are displayed in Figure 2.2. Peak flow frequencies for this record period since 1938 are presented in Figure 2.3.

The City of Monroe maintains a stream flow gauge in the River Raisin at Dam #1 (second low head dam relative to the river mouth). This gauge is located in the City of Monroe approximately 152 m downstream from Maple

Avenue (Petty, 1984). Daily readings are recorded by the Monroe Waste Treatment Plant (WWTP).

The lake level is monitored hourly by three National Oceanographic and Atmospheric Administration (NOAA) gauges located near the study area. Water stage readings for Gage 3087 in the turning basin are presented in Figure 2.4 (January 1, 1975 to March 31, 1983). The other two gauges are located on Lake

Erie at Toledo, Ohio (Station 3085) and the Fermi Power Plant, Stony Point, Michigan (Station 3090).

The port of Monroe is served by a dredged channel 15,800 feet (4.8 km) long, 300 feet (91.2 m) wide and 21 feet (6.4 m) deep from Lake Erie to the mouth of the River Raisin. From the river mouth to the turning basin, there is a dredged channel 8,200 feet (2.5 Km) long and 200 feet (60.8 m) wide (Michigan DNR, 1979). See Figures 2.5 and 2.6 for depth contour maps.

2.3 INDUSTRIAL DEVELOPMENT

Most of the River Raisin is in agricultural production. Over 70% of Lewanee and Monroe Counties are farmed.

Urban development of the basin is centered around three cities: Monroe, Adrian and Tecumseh. Monroe, at the River Raisin mouth is the most populuous and industrialized city in the basin. A 1980 census listed Monroe as having a population of 23,531. Much of the industry is associated with automobile manufacturing in nearby Detroit. Additional industries in the area are primary metals, fabrication of metal products, machinery and transportation equipment, manufacture of paper products, chemicals, furniture, food processing and dairy related industries (Michigan DNR, 1979).

Several paper product companies are located on the River Raisin within the study area. Consolidated Packaging Corporation, South and North Plant closed on February 1978 and July 1975, respectively (Figure 2.7). Their products were corrugated and solid fiber containers. Time Container Company, a paper products industry, is located upstream of the study site near the Chesapeake and Ohio Railroad. Union Camp Corporation on the north shore of the River Raisin produces corrugated paper board and containers. The effluents from the primary treatment facilities of both Time Container and Union Camp are sent to the Monroe WWTP for secondary treatment (Michigan Department of Public Health and the Michigan Water Resources Commission, 1969).

The Detroit Edison Plant is located near the mouth of the River Raisin on the south side of the river. This fossil-fueled, steam-electric power plant has an exceptionally large, once-through cooling system. Up to 85 m^3/sec of water are pumped for cooling purposes. A map of the plant in Figure 2.8 shows the intake and discharge channels (Cole, 1978).

During spring runoff, the River Raisin makes up more than 95% of the cooling water. However, during low flow in the summer, the river makes up less than 5%, the balance of water is from Lake Erie. Water enters the cooling system through a 100 meter-long intake canal that is located about 650 meters upstream from the river mouth. After water passes through the condenser, it is released into a 350-meter long, concrete conduit where water velocities are approximately 1 m/sec at full operation. The water is then discharged through a rock-walled canal averaging 175-meters wide. Plum Creek joins the discharge canal, but contributes less than 1% of the volumetric flow to Lake Erie. The average annual river discharge is equivalent to 20%

of the total cooling water demand - the rest is drawn from Lake Erie (Cole, 1978).

The Monroe Metropolitan Water Pollution Control Facility is located on the south bank of the River Raisin. The plant receives raw wastewater from the City of Monroe, Frenchtown Township and Monroe Township. Under normal operating conditions, all wastewater flows are conveyed to the treatment plant. Under severe runoff conditions, high flows in the collection system exceed the plant capacity. During this time, untreated wastewater is pumped directly into the River Raisin from the Flood Pumping Station. The present treatment facility can adequately provide secondary treatment for flows up to 30 MGD (113,550 m^3). Sludge disposal is through a contract arrangement with disposal in the State of Ohio (Monroe County Drain Commission, 1984).

2.4 CONTAMINANT SOURCES

Both toxic contaminant reserves in sediments and current toxic chemical loadings to the River Raisin from existing industrial, municipal and landfill activities were considered as potential sources of toxins in the Monroe Harbor study.

Copper, chromium, and zinc were analyzed in the study because of the relatively high concentrations of these metals found in sediments in the River Raisin and because of the toxic nature of these metals to cladocerans and other freshwater invertebrates. Relatively high levels of toxic heavy metals in the navigation channel have been reported in the literature. The USEPA Great Lakes Surveillance Branch (1975) recommended that the contaminated dredged sediments from the navigation channel should not be disposed in the open lake. Among other contaminants, their analysis revealed high levels of copper (1450 mg/kg), zinc (970 mg/kg), and chromium (530

mg/kg). Based on atomic absorption spectroscopy (AAS) by Cranbrook Institute of Science and neutron activation analysis by the University of Michigan's Phoenix Memorial Laboratory (Jones, 1983), concentrations of these metals were relatively high when compared to mean sediment levels in southern Lake Huron. Concentrations of some other metal also were found to be relatively high in these studies, but their toxicity at these levels to freshwater biota was negligible or unknown. In addition, several metals were excluded from the Monroe Harbor study because of economic and instrumental limitations at the EPA Large Lakes Research Station.

In addition to reserves of metals in the sediment, there is an existing potential for heavy metal discharge from primary metal production, plating, and metal machining industries in the Monroe Harbor area.

Polychlorinated biphenyls (PCBs) were included in the study of Monroe Harbor because high levels of PCBs in fish were found in the area. In 1971, the Michigan Department of Natural Resources collected fish in the River Raisin and found up to 6.45 mg/kg of Aroclor 1254 in northern pike (wet weight) and up to 3.08 mg/kg of Aroclor 1254 in carp (wet weight). The results of a 1979 survey included a single carp with 77.2 mg/kg of total PCB (MDNR, personal communication).

PCBs have been linked to industrial activity that use the persistant compounds in lubricants and coolants for electrical equipment. PCBs have also been found to be a by-product in paper recycling plants. These industrial uses and processes exist (or existed) in the River Raisin study area; therefore, it is possible that the sediment and fish contamination observed originated from local industrial activity.

3.0 APPROACH AND METHODS

3.1 SAMPLING RATIONALE AND STRATEGY

The approach to sampling design for water chemistry in the River Raisin - Monroe Harbor estuary was based on the need to address multiple objectives (as defined in the previous section) with limited resources. Spatial and temporal gradients in water chemistry were viewed as important elements in sampling designed to provide data for:

1) An integrated approach among physics, chemistry, and biology;

2) A mass balance of various chemicals;

3) An assessment of water quality during critical events.

The strategy for sampling, then, was to attempt to obtain this gradient information on various surveys throughout the study in ways that would meet as many of these objectives as possible.

All of the surveys were designed with the integrated approach in mind. Water chemistry samples were taken simultaneously with water movement measurement and renewal water for biological testing. This ensured the compatability of the data. The first few surveys were quite extensive in space and time, allowing the needs of the integrated approach and the mass balance to be met. As preliminary information from these surveys became available, the sampling was tailored to the types of information still lacking. For example, results from the first three surveys guided the next three surveys in which the effects of critical events were defined. Thus,

the strategy was a flexible one, in that it took advantage of knowledge gained in the previous surveys as well as seasonal changes at the sampling site to address information gaps as the study progressed.

Over the course of the two years of the Monroe Harbor study, the sampling strategies and locations were altered to reflect increasing understanding of the ecosystem, and to account for seasonal changes in water flow and discharge (see Tables 3.1 and 3.2). These different approaches are described below.

Surveys I and II (July 12-17 and September 13-18, 1983)

The purpose of these surveys was to investigate the presumed existence of a contaminant/toxicity gradient within the lower River Raisin ecosystem. Total and dissolved metals and organics were sampled at five river stations, one tributary (Mason Run) and one Lake Erie station. In addition, total and dissolved metals and total organics were collected from four potential point sources (see Figures 3.1 and 3.2). During Survey I, daily grab (once/day) and composite (three times/day, and combined) samples were collected at all stations. During Survey II, composite samples were collected at selected stations, which changed each day. In addition, grab samples were collected at half of the stations each day, with the locations changing so that each station was sampled every other day.

Survey III (October 25-28, 1983)

Based on the results of the *Ceriodaphnia* and fathead minnow toxicity tests associated with Surveys I and II, attention was focused on the effluent plume of the Monroe Waste Water Treatment Plant (WWTP), from its discharge pipe downstream to the turning basin (see Figure 3.3). The purpose of this

plume study was to sample a stronger, more well-defined gradient of water quality and toxicity for correlation analysis.

Daily grab samples, for total and dissolved metals and total organics, were collected at all plume stations, and dissolved organics samples were collected from a subset of the plume stations and from Lake Erie. To provide continuity with previous work, on the first day of the survey composite total and dissolved metals and organics samples were also collected from all of the stations used in Surveys I and II.

Survey IV (April 2-5, 1984)

With this survey, the scope of the Monroe Harbor project was expanded to include the nearshore zone of western Lake Erie. Aerial observation showed that the runoff-fed, highly turbid and discrete River Raisin plume extended out into Lake Erie, with its exact direction and extent largely determined by prevailing wind patterns.

On April 4, 1984, subsurface samples for total and dissolved metals and total and particulate organics were collected at eight river stations, two tributaries, one potential point source (WWTP), and ten nearshore Lake Erie stations. In addition, similar samples were collected from a depth of three meters at four of the river stations. See Figures 3.4A and 3.4B.

Survey V (May 9, 1984)

Like Survey IV, this survey included an evaluation of the contaminant gradient in the River Raisin plume as it was diluted and dissipated in the nearshore zone of Lake Erie.

Seven stations were positioned in Lake Erie along a temperature/-conductivity gradient established on the day of the survey. Total and

dissolved metals grab samples were collected at these stations and also at one tributary, one point source, and three river stations. Total and particulate organics grab samples only were collected from two river stations, 1 and 4. See Figures 3.5A and 3.5B.

Surveys VI, VII, VIII, IX and X (May 30, June 12, July 10, July 25 and August 1, 1984)

These surveys were intended to evaluate the temporal variability of contaminant concentrations and their associated toxicities within the River Raisin. Total and particulate organics grab samples were collected at two river stations, 1 and 4. Total and dissolved metals samples were collected at these stations, at the mouth of the river (26) and at the mouth of the Detroit Edison power plant coolant water discharge canal (29). See Figure 3.6 for details.

3.2 COLLECTIONS

Any project of this scope requires a sampling strategy that will provide a maximum amount of information while still taking personnel and analytical constraints into account. With this in mind, the water sampling efforts were divided between two sample types:

- Grab samples, that provided "snapshots" of contaminant concentrations at a specific instant in time; and
- Composite samples, that gave an average, integrated value of contaminant concentration over a known length of time.

Organics and metals grab samples were collected on all surveys, as described in Section II of this report. Sample volumes for organics varied; 4 L for Surveys I and II, 8 L for Survey III, and 12 L for the remaining surveys. This reflected our estimation of expected contaminant levels.

Composite samples were collected only on Surveys I, II and III. Every eight hours (0800, 1600 and 2400 hours) on each day of the survey, water was collected, returned to the USEPA R/V Bluewater and processed as described in Sections 3.1.A and B. For organics analysis, solvent extracts from each part of the composite (1 L) were collected in the same bottle, resulting in a 3 L composite sample representing one 24-hour period. For metals analysis, splits of each part of the composite were also combined in the same bottle.

In addition to collecting both grab and composite samples, the whole water was often fractionated into dissolved constituents and particulates. Details of the processing of these fractions are described below.

3.2.1 Total (Whole) Water

Organics

Sample volumes varied depending on survey number and sample type. Each 1 L sample was collected in a 1-gallon (3.8 L) amber glass jug (empty Burdick & Jackson pesticide-grade solvent bottle). Near-surface samples were collected by submerging the bottles by hand. Sub-surface water was collected by a portable peristaltic pump equipped with silicone pump tubing and Tygon® (polyvinyl chloride, PVC) sampling hose.

The bottles were returned to the USEPA R/V Bluewater, which was anchored near Station 4. One hundred milliliters (mL) of dichloromethane (DCM) was added to each bottle, and they were shaken vigorously for three minutes. After waiting two hours for the solvent to settle, the DCM layer was drawn off using a one liter separatory funnel. An additional 100 mL DCM was added to the sample, which was again shaken for three minutes; after a brief settling period, the DCM was added to the first extract via the

separatory funnel. The water was discarded, and the jug rinsed with 50 mL DCM. This rinse also was added to the extract. This solvent extract was stored in a 1-gallon amber glass jug in the dark at room temperature until further processing occurred at LLRS, as described in Section 3.3.

Metals

Trace metal samples were collected in new wide-mouth 500 mL Nalgene® linear polyethylene (LPE) bottles washed with hot water in a dishwater, rinsed with deionized water, with 30% v/v nitric acid, and again with deionized water; bottles were then soaked in 2% v/v nitric acid for two weeks, rinsed six times with deionized water, and dried in an oven (105°C) with the caps ajar.

Near-shore river samples were collected by hand. The bottle was quickly lowered below the water surface and filled, after a prior rinse with station water. On several occasions, Station 4 was sampled near the bottom. Sampling these lower levels required a peristaltic pump equipped with silicone pump tubing and a TYGON® sampling hose.

Effluents and tributaries were sampled by several methods. Mason Run was sampled from a bridge (Station 8) by lowering a half gallon LPE wide-mouth Nalgene® bottle fixed to a polypropylene rope with stainless steel clamps. The bottle was weighted from below with lead, and the bottle mouth was sheltered with a plastic awning or lid suspended from the rope just above it. The purpose of the lid was to keep out debris as the sample was pulled up. Before sampling, the bottle was rinsed with station water. This technique was also used when the Ford intake (Station 10) was sampled. Hand dipping was the method used to collect water at Ford's polishing lagoon

(Station 9). The Monroe Wastewater Treatment Plant (Station 7) was sampled with the peristaltic pump apparatus.

All total metal samples were acid-spiked and stored in 500 mL polyethylene bottles.

3.2.2 Filtered Water (Dissolved Fraction)

Organics

Bottles of raw water were returned from the field to the R/V Bluewater, and the water was pumped (Cole-Palmer 1/3 h.p. peristaltic pump; 5/16 inch (i.d.) silicone and Teflon® tubing) through a 1,000 μm stainless steel prefilter and a prebaked (482°C) Whatman GF/F glass fiber filter (4.25 cm diameter; 0.7 μm porosity) into a 1-gallon amber glass bottle. Filters were changed when the back pressure reached 10 to 15 p.s.i. One to six filters were used per sample. The pump was purged thoroughly with sample water between samples. One hundred mL of DCM was added to each filtered sample. The sample was extracted as described above for whole water. Volumes filtered ranged from 3 to 8 L.

These filtered water extracts were stored as per the total water extracts.

Metals

A 100 mL portion of the unacidified total metal sample was filtered through a 0.45 μm Sartorius cellulose acetate filter. The filtering apparatus was a Millipore polycarbonate Sterifil® filtration system. Before use, the system was soaked in 4% v/v HNO_3, then rinsed well with deionized water. The filter was set in place and 50 mL of deionized water was filtered, then discarded. Fifty mL of sample was then filtered and discarded. Sample water was filtered until the filter began to clog. Before

filling a 175 mL LPE bottle with filtrate, the first 50 mL of filtrate was used to rinse it out.

When filtering was complete, both the total and dissolved samples were preserved with ULTREX® nitric acid by adding 3 mL per liter of sample. Samples were refrigerated at 7°C until analyzed.

3.2.3 Particulates

Organics

After Survey III (the last survey of 1983), it was realized that the collection of filtered water by the method described above presented a number of difficulties. First, frequent filter changes required by the high turbidity at some stations increased the level of background contamination. Also, the small sample volume necessitated by time and equipment constraints sometimes did not provide adequate contaminant levels for analysis. Consequently, the amount of dissolved PCB was calculated indirectly, by collection and analysis of the suspended particulates and whole water, rather than directly by analysis of the filtrate.

In this procedure, whole water was collected in glass jugs as in previous surveys, and transported back to LLRS. The water, pumped by a peristaltic pump equipped with silicone rubber pump tubing and approximately 1.5 m of 9 mm (i.d.) Teflon® sample tubing, was passed through a stainless steel filter-holding apparatus containing a 1,000 µm prefilter and a 0.7 µm-porosity, 293 mm-diameter Whatman GF/F glass microfiber filter (prebaked at 482°C). The filtrate was collected for volume determination. Filtration was stopped when the back pressure reached approximately 10 p.s.i. (70 kpa). The filter was removed, folded, and placed in a clean (soap and water; acetone, DCM and hexane rinse) flint glass jar containing 150 mL

acetone. Jars were stored in the dark at 8°C until extraction. Between samples, the apparatus was purged with water from the next sample for approximately 30 seconds. Separate filtration equipment was used for river, point source and Lake Erie samples to minimize "carry-over" contamination.

Volumes filtered ranged from 4 L to 16 L, depending on particulate concentrations.

3.3 SAMPLE EXTRACTION

3.3.1 Total and Filtered Water

The solvent extracts collected in the field were returned to LLRS. The extract was poured from the bottle into a one-liter separatory funnel, passed through an anhydrous sodium sulfate column and into a 500 mL Kuderna-Danish (KD)/lower tube assembly. When half full, the KD and a Snyder column were placed on a steam bath and the solvent was concentrated to approximately 50 mL. This concentration was repeated until all of the DCM extract had been reduced to approximately 50 mL. A rinse of 250 mL n-hexane was then run through the separatory funnel and sulfate column and into the KD, and the solvent was then boiled down to less than 10 mL.

The concentrated hexane extract was transferred to a 10 mL graduated tube and then evaporated in a water bath under nitrogen gas to 0.5 mL. This was then diluted to 2.0 mL with hexane.

The extract was then either left in the graduated tube for cleanup with concentrated sulfuric acid, or pipetted into an ampule, sealed and stored for Florisil® cleanup (Section 3.4).

System blanks consisted of a volume of DCM equal to that used to extract the largest sample of each set.

3.3.2 Particulates

The contents of the jar (filter and acetone) were placed in the Soxhlet apparatus (Soxhlet, 500 mL roundbottom flask and condenser) and extracted with 150 mL n-hexane and 150 mL acetone for six hours on a heating mantle. Extract was poured from the roundbottom flask into a KD flask and concentrated to 50 mL on a steam bath. n-Hexane (100 mL) was added to the KD, and again concentrated to 50 mL. The extract was poured into a separatory funnel, as was an n-hexane rinse of the KD. Any lower water layer was drained off and discarded, and the extract was passed through an anhydrous sodium sulfate column into the KD. Another 100 mL of hexane was passed through the same separatory funnel and sulfate column and into the KD. The extract was finally concentrated to less than 10 mL on the steam bath.

The extract was then transferred to a 10 mL graduated tube and evaporated in a water bath under N_2 gas to 0.5 mL. n-Hexane was added to restore it to 2.0 mL.

Extract cleanup was as described below.

System blanks consisted of unused filters placed (in the field) in a clean jar with acetone, and processed as per the sample filters.

3.4 CLEAN-UP (ORGANICS)

All organic total water, filtered water, and particulate sample extracts were acid cleaned. Four mLs of concentrated H_2SO_4 (Baker Instra-Analyzed®) was added to the graduated tubes containing the extract, shaken, and allowed to sit overnight. The following morning the graduated tubes were placed in an acetone/dry ice bath until the acid layer froze, at which time the upper n-hexane layer was pipetted off, placed in an ampule and sealed.

In addition to acid clean-up, some total water and all particulate samples from Survey 4 required further clean-up with Florisil®.

Clean-up columns were dry packed with 20 grams of Florisil® which had been baked at 650°C for two hours and stored until needed in a 130°C drying oven.

After an initial 50 mL rinse of the column with n-hexane, 1 mL of sample extract was injected onto the column followed by 250 mL of 4% DCM in hexane.

The eluant was collected in a KD flask, concentrated to less than 10 mL on a steam bath, and transferred to a 10 mL graduated tube. A stream of N_2 gas was used to evaporate the eluant down to 0.5 mL, after which it was brought up to 2 mL with hexane, transferred to an ampule and sealed.

A blank and a PCB standard were processed with each Florisil® group and were treated as samples with the following exceptions: 1) no initial extract was injected onto the column for the blanks; 2) 2 mL of PCB standard was injected onto the column; 3) 200 µL of of internal standard was added to both the blank and the standard before the final volume was adjusted to 2 mL with n-hexane.

In addition, 2 mL of PCB standard solution obtained from the same batch as the standards eluted through the column, was evaporated to 0.5 mL with nitrogen, 200 µL of internal standard was added and the final volume was adjusted to 2 mL with n-hexane.

3.5 ANALYSIS AND QUANTITATION

3.5.1 Organics

High resolution fused silica capillary gas chromatography was performed on a VARIAN Model 3700 gas chromatograph equipped with a ^{63}Ni

electron capture detector (ECD). A 50 m fused silica column (0.2 mm i.d.) coated with SE-54 (Hewlett-Packard) was used to separate the PCB congeners. The oven temperature was programmed at a rate of 1.0°C min^{-1} from 100 to 270°C and held at 270°C for ten minutes. The injector and detector temperatures were 270°C and 320°C, respectively. The sample volume, 4.5 µL, was injected by an automatic sampler using a splitless injection technique (10:1 split ratio, vented from 0.75 to 1.75 min). The hydrogen carrier gas was held at a constant pressure of 2.25 kg cm^{-2} to give the optimized velocity ($\bar{u}$) at 100°C of 50 cm sec^{-1}.

The chromatographic data were acquired using a Hewlett-Packard 3354 Laboratory Automation System (LAS) and transferred to a Digital PDP-11/45 computer via magnetic tape.

Once transferred, each raw file was subjected to a series of programs for data analysis:

(1) Attenuate (ATN) - Expands the scale of the chromatogram.

(2) PLOT (PLT) - Establishes a chromatogram base line.

(3) PEAKS (PKS) - Determines peak height.

(4) Mean Standard Deviation (MSD) - Determines baseline noise mean and the standard deviation used in the 'Peaks' program.

(5) PUP - Compares the sample file to a library file for retention time and names PCB or Pesticide peaks detected.

(6) UPDATE (UPD) - Updates the library with the calibrating standard.

(7) Sample Final Concentration (SFC) - Gives the total PCB or Pesticide sample concentration, the number of peaks accepted in the analysis and the homolog distribution

(8) COMSTAR (CMS) - A multiple regression program that fits observed congeners in sample with a linear combination or Aroclors. Any peaks not fit are considered outliers and marked for rejection.

Once the analysis was completed, the data were stored in a final data base and archived on magnetic tapes.

3.5.2 Metals

Because suspended particulates were present, all total metals samples were nitric acid digested using a method adapted from USEPA (1971).

Copper and chromium were analyzed with a Perkin-Elmer 460 Atomic Absorption Spectrophotometer fitted with a graphite furnace, a HGA-220 controller and AS-1 Auto Sampler. Analytical conditions were determined by applying the methods in Perkin-Elmer (1977).

Duplicate injections and analyses were performed on each sample, blank, and standard. The mean peak height was used to calculate the concentration.

Zinc, because of its higher concentrations, was analyzed using a Perkin-Elmer 603 Atomic Absorption Spectrophotometer in the flame mode. Standard grade acetylene and air were used to support the flame. Analytical conditions were taken directly from the Perkin-Elmer 603 Methods Manual.

After absorbance readings or peak heights were measured, the data were processed automatically using a computer program which was written to correct for blanks, perform linear regressions, plot the standards, and determine the concentration of the samples.

Detection limits for the metals analyzed are reported in Table 3.3.

3.6 QUALITY ASSURANCE

The quality assurance program was designed to control and evaluate the quality of field and laboratory work with respect to: (a) accuracy, through analysis of blanks and standards, intercomparison and sample recovery

studies; and (b) precision, through replicate and between-run analyses. The specific uses of these quality control measures are described below.

3.6.1 Metals

Any analytical procedure should address accuracy and precision of the measurement. Trace metal analyses are subject to various sources of error, which complicates interpretation of the final results. Not knowing the precision of measurements limits the usefulness of the data set.

To insure accuracy, blanks were quantified at various steps in the analytical process (Table 3.4). The filtering process in the field was monitored by filtering deionized water. This sample served as a filter blank. Sample bottles used in the study were tested for blank levels by filling them with deionized water and preserving and storing them with the field samples. The metals digestion process was monitored by digesting three deionized water blanks for every 20 samples. These blanks were used to correct the sample concentration results as shown in Section 4.6.

Accuracy of the results was also insured by use of intercomparison samples (Table 3.5). These samples were received from the United States Environmental Monitoring and Support Laboratory, Cincinnati. Intercomparison samples helped insure accuracy by comparing our analytical results to outside measurements.

Standard additions were used to quantify samples whenever recovery of the added metal was not close to 100%. Some metal analyses, such as for lead, are more prone to recovery problems in the laboratory than are others. The approach taken in this project was to assume that recovery would be a problem whenever samples from a new study site were received. Therefore, all samples were quantified initially by the standard addition method.

After a number of analyses were performed, the recoveries were evaluated (Table 3.6). Standard additions were continued for any metal analyses with persistent recovery problems. Metal analyses without recovery problems were measured by directly comparing analytical absorbance signals to a standard curve.

Precision was estimated at various stages of the analytical process. Duplicate samples were collected in the field. Analytical results from these duplicates provided the data user with an estimate of overall variability in the analytical process, which included variability in the medium sampled (Tables 3.7, 3.8). Analytical/instrumental variability included variability of sample handling in the laboratory and uncertainty from analytical instrumentation. This analytical/instrumental precision was estimated by using between-run sample replicates, defined as the standard deviation of a sample analyzed each for some period (Table 3.9).

In order to determine contamination introduced in the filtering process, two filter blanks were taken during each eight-hour shift in the field. This involved filtering a sample-sized volume of deionized water. An unfiltered sample of deionized water was also taken at the same time. The unfiltered sample (batch blank) served two purposes: as a bottle blank, and as a reference for the filter blank. The analytical results of the batch blank and filter blank were compared; if equal, they were then no filter contamination was recorded. Equality here was confirmed by a T-test (Table 3.4).

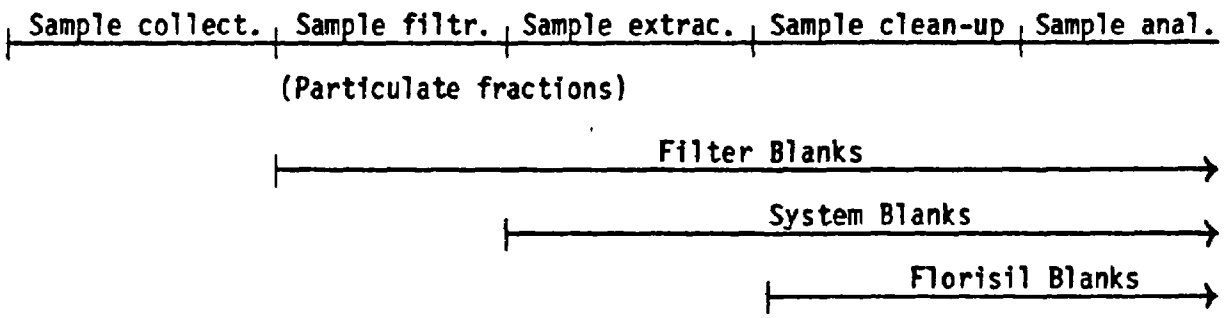
3.6.2 Organics

A quality assurance plan was designed and used here to address method interference, particulate extraction efficiency, precision and accuracy.

Method Interference

The preparation of organic samples for gas chromatographic analysis is a complex process involving many steps. An effort was made not only to monitor overall method interference but also to determine at what processing step(s) interferences were introduced when they did occur.

The figure below shows the steps monitored by each type of method interference check blank.



A filter blank consisted of an unused filter stored in a clean jar to which 150 mL of acetone was added. The filter blank was then processed along with particulate samples.

Each extraction group had an associated system blank which represented a volume of DCM equal to that used to extract the largest sample. This blank was then processed as a sample.

Florisil® blanks were used to monitor possible contamination from the Florisil® clean-up procedure. Florisil® blanks were processed along with each clean-up group and were treated as samples with the exception that no initial extract was injected onto the columns.

Comparison of filter blanks, system blanks and Florisil® blanks indicate at which point in the process and at what levels method interferences occurred.

In order to evaluate filter extraction efficiency, four particulate filters were extracted for six hours, the solvent was changed, and the filters were extracted for an additional sixteen hours. Both first and second extracts were analyzed. Efficiency of extraction was calculated by dividing the value of the first extract by the sum of the values of the first and second extracts and multiplying the result by 100 (Table 3.10). An assumption was made that extraction for a total of 22 hours removed all of the extractable material.

Precision

Precision was estimated for the entire measurement system using collocated duplicate samples (Table 3.11).

Analytical precision was estimated by repetitive analysis of PCB calibration standards analyzed as samples (Table 3.12).

Accuracy

Instrumental accuracy was assessed by analyzing Aroclor mixtures 1221, 1016, 1254 and 1262, obtained from the U.S. Environmental Protection Agency's Monitoring and Support Lab (EMSL), Cincinnati, Ohio (Table 3.13).

4.0 RESULTS AND DISCUSSION

Results are presented in terms of spatial and temporal profiles of PCB concentrations in whole water and particulate samples, and of chromium, copper and zinc concentrations in whole water and filtrate samples (Figures 4.1 - 4.41). The numerical values plotted in the profiles are also given in Tables 4.1 - 4.9, along with PCB analysis blanks. In the metals data, blank values have already been subtracted from sample measurements. PCB analysis was performed at the level of specific congeners and homologs, but only the total PCB results are reported here. Calculations of "dissolved" PCB and "particulate" metals concentrations can be made from these data. The same applies to the metals data.

The organochlorine analysis included other selected compounds: pentachlorobenzene, alpha-BHC, hexachlorobenzene, gamma-BHC, heptachlor, alpha-chlordene, aldrin, gamma-chlordene, heptachlor epoxide, oxychlordane, gamma-chlordane, alpha-chlordane, trans-nonachlor, dieldrin, 4,4'-DDE, endrin, cis-nonachlor, 4,4'-DDD, 4,4'-DDT and methoxychlor. Since concentrations of these were not exceptional, the results are not included in this report.

Spatial profiles reflect gradients of PCB or metal concentrations in the water column along a series of stations from the upstream boundary of the study area (Station 1) to the nearshore waters of Lake Erie (Station 11). As indicated on the maps (Figures 2.1 - 2.6), the stations include point

sources of contaminants, surface and bottom water samples at Station 4, and plume gradients. The mean concentrations given below for each survey represent both composite and grab samples, and duplicate samples that were collected in some cases over several days.

Temporal profiles show seasonal variations of PCB or metal concentrations in the water column at only two locations, Station 1 at the upstream boundary, and Station 4 just downstream from the turning basin (Figure 2.1). Ten surveys were conducted during July 1983 through August 1984. Profiles of river flow conditions during the surveys are shown in Appendix A (Figures A.1 - A.10).

Quality control results are given at the end of the separate discussions of organics and metals.

4.1 SPATIAL PROFILES, PCBs

For Survey 1 (July 12-17, 1983) a comparison of whole water data for composite and grab samples is presented in Figure 4.1. Each plot of mean, standard deviation and range represents five days of samples (generally five composite samples and two grab samples). Both profiles reflect similar gradients of total PCB concentrations which occurred at Station 8 and 4 near the turning basin. The actual values for composite and grab samples are given in Table 4.1. For most of the 24-hour periods, the composite sample value was slightly higher than its grab sample counterpart (average of 33 vs. 30 ng/L). All composite and grab sample values during Survey 1 have been combined for each station as shown at the bottom of Table 4.1. The mean values indicate that total PCB concentrations near the upstream boundary (Station 1) were on the order of 7-9 ng/L. The discharge water from the Monroe Waste Water Treatment Plant (Station 7) was markedly higher at 34

ng/L. Apparently, this effluent level was reduced to 8.9 ng/L by dilution just downstream from the plant at Station 3. Mean PCB concentrations further downstream were dramatically higher at 147 ng/L in the mouth of Mason Run (Station 8) and at 51 ng/L just below the turning basin (Station 4). High variability at these stations indicates some episodic effect on PCB concentrations. Levels were elevated to 57 ng/L also at the water intake of a large automotive plant (Station 10) nearby. However, in Lake Erie near the River Raisin mouth (Station 6), the PCB level of 14 ng/L was much reduced, and was near the boundary condition level of 9 ng/L at Station 11 approximately 5 km offshore. Additional samples from Stations 7, 9 and 5 required further clean-up before analysis, and these results are not yet available.

Results from some corresponding composite filtrate samples (Figure and Table 4.2) indicate first, that in most cases the filtrate values were unrealistically higher than the totals and were, therefore, contaminated. Because of later concern about contamination in the filtering process and the likelihood of low filtrate values being near detection limits, particulate fractions were collected instead of filtrate after the first three surveys.

In Survey 2 (September 13-17, 1983), the sampling plan differed somewhat. Station 2 was dropped because it seemed to duplicate conditions at Station 1. No results are available for Station 7. Station 4 was sampled at 1 m and 1 m above the bottom in order to evaluate any effects of stratification. The results of Survey 2 (Figure and Table 4.3) indicate a similar spatial pattern of PCB distribution except that concentrations were much higher relative to boundary conditions of 10 ng/L. PCB levels in the lower river and nearshore lake were approximately double those in the

previous survey. At Station 4, the PCB level in surface water was some 30% higher than that near the bottom. As in Survey 1, filtrate samples were contaminated by the filtering process and did not yield reliable results.

Survey 3 (October 25-27, 1983) involved two different strategies. Results of the first phase consist of a composite sample profile of the same station as used in Survey 1 and 2 (Figure and Table 4.4). The station profile of PCB is again similar to that in previous surveys except for an anomalous value of 220 ng/L in offshore Lake Erie (Station 11) whole water. The comparable filtrate value (9.2 ng/L) is more realistic. Filtrate values as a fraction of whole water PCB are shown in Table 4.4(B). Not counting the upper and lower extremes, the average of filtrate/whole water PCB was 53%. In the second phase of the survey, PCB profiles were recorded over three days by daily grab samples taken at seven new stations within the Monroe WWTP effluent plume (Figure 2.3). The results (Figure and Table 4.5) defined a downstream gradient of PCB that was generally weak but more pronounced along the south shore of the river. Sharp rises in concentration observed at Station 19 on days 1 and 3 of the survey probably indicated the influence of much higher levels seen in the turning basin during the first phase, especially in surface waters. Within the plume group of samples, several of the filtrate values exceeded those of whole water (Figure and Table 4.6).

In Survey 4 (April 2-5, 1984) whole water and particulate grab samples were collected at most of the original and some additional stations as well (Figure and Table 4.7). The new stations were established to monitor the dispersion of contaminants within the river plume in nearshore Lake Erie during a period of high runoff and river flow. However, most of the lake samples required further clean-up, and the results were not available here.

In the river profile PCB levels exhibited the usual increases in the area of the turning basin and declines toward the river mouth and into Lake Erie. The Edison Power Plant inlet in the lower river (Station 24) and outlet in the lake (Station 29) had similar concentrations of whole water PCB at 17 and 19 ng/L. Although particulate PCB values were approximately half that of whole water in most cases, they exceeded whole water values in four samples. Most significantly in Survey 4, the PCB concentrations at Stations 8 (Mason Run) and 4 (below turning basin) were much lower than in previous low-water surveys. Most values in this area (at 13-31 ng/L) were not markedly higher than the upstream boundary or lake concentrations; this suggests a greater dilution effect with increased flows.

In Survey 5 (May 9, 1984) the sampling strategy of Survey 4 was repeated on the lower river and its plume in nearshore Lake Erie. Although metals analysis was conducted on all samples, PCB analysis was limited to whole water and particulate samples from Stations 1 and 4 only. These two stations represented the upstream boundary condition and outflow from the turning basin, respectively. Due to analytical constraints on PCB analysis, this approach was continued throughout the remaining surveys. Surveys 6-10 were conducted on May 30, June 12, July 10, July 25 and August 1, 1984. On these latter five surveys, Stations 1, 4, 26 and 29 were sampled for whole water and dissolved metals. Only Station 1 and 4 were sampled for whole water and particulate PCB.

4.2 TEMPORAL PROFILES, PCB

The PCB results for Surveys 5-10 (Figures and Tables 4.8 and 4.9) are presented here as a temporal profile of concentrations at Station 1 and 4. Concentrations in river water entering the study area at Station 1 appeared

to reach a maximum of 13 ng/L in late May, and declined steadily to a season low of 4.3-4.6 by August 1. Particulate PCB levels averaged slightly less than half of those in whole water. In contrast, PCB concentrations at Station 4 showed an opposite tendency to reach a minimum of 7-14 ng/L in May and June, and increased to a maximum value of 210 ng/L on August 1. These trends suggest that the levels of PCBs below the turning basin may be inversely related to concentrations upstream.

Other temporal profiles for Stations 1 and 4 (Figures 4.10 and 4.11) represent all of the grab and composite sample data for ten surveys in 1983-84. The results for Station 1 indicate fairly consistent levels of PCB, mostly in the range of 5-15 ng/L, during the fall and spring. The lowest concentration of ∿3 ng/L occurred in early October, 1983 (Survey 3). This was in a period of low flow (∿5 cm/sec), as were the highest concentrations of 13 ng/L during Survey 2. At Station 4, however, the highest levels of 600 ng/L in Survey 2 at low flow were 3-fold greater than any values observed during similar low flow conditions in Surveys 8-10. Since concentrations do not seem well correlated to flows or upstream PCB levels, this suggests some change in the sources of PCB in Station 4 water between fall 1983 and spring 1984. One possible influence is the maintenance dredging that occurred during this period, or a change in external loadings to the turning basin.

A summary of PCB data from selected stations for all 10 surveys is shown in Table 4.20.

4.3 ORGANICS QC

Blank values have not been subtracted from the organics data, but are presented separately here.

Method Interference

System blanks, filter blanks and Florisil® blanks are reported as the percent the blank value was of the associated sample values (Tables 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, and 4.9).

Of 156 total water composite and grab samples analyzed with associated system blanks, 85% had system blanks ≤10% of the total sample values, and only 4% had system blank values in excess of 50% of the associated sample values.

All of the system blank values exceeding 50% of the corresponding sample values were composite samples from Survey 3.

Ninety-five percent of filtrate water samples analyzed with associated blanks had system blanks ≤10% of the total sample values while 81% of particulate samples had filter blanks ≤10% of the corresponding sample values.

Thirteen particulate samples from Survey 4 were Florisil® cleaned and thus had associated Florisil® blanks. All 13 samples had Florisil® blanks which were _11% of the associated sample values.

Particulate Extraction Efficiency

Four particulate samples were processed and analyzed to determine particulate extraction efficiency. The results indicate that the extraction was both highly efficient and reproducible (Table 3.8).

Precision

Results of the analysis of collocated duplicate samples are shown in Table 3.9.

Although one of every ten samples was collected in duplicate, due to sample selection for analyses, instrument and processing problems, less than ten percent of the samples analyzed were duplicates.

The replicate analysis of PCB calibration standards for analytical precision showed mean values within ± 10% of the true concentrations (Table 3.10).

Accuracy

Instrumental accuracy was monitored by analyzing Aroclor mixtures (Table 3.11). Aroclor mixtures 1016 and 1262 consistently showed values higher than the true concentrations.

4.4 SPATIAL PROFILES, METALS

Results for copper, chromium and zinc, as totals and dissolved fractions in water, are presented as a series of spatial profiles representing the river and lake stations discussed earlier (Figures 4.12-4.39 and Tables 4.10-4.19). The following general observations pertain to the results of each survey.

In Survey 1 (Figures 4.12-4.14, Table 4.10), mean zinc concentrations were particularly high at Station 7 (43.4 μg/L) and Station 9 (80.3 μg/L). The latter represented effluent water discharged by a large automotive plant. Copper and chromium levels (42 μg/L and 32 μg/L) were also relatively high at Station 9. By comparison, the upstream boundary mean concentrations of copper, chromium and zinc at Station 1 were 3.87, 1.59 and 4.14 μg/L, respectively. The open lake values at Station 11 were still lower at 2.75, .933 and 3.17 μg/L, respectively. Slightly elevated levels of all three metals were also observed at Station 8 (Mason Run) and Station 10 (the auto plant water intake).

In Survey 2 (Figures 4.15-4.17, Table 4.11), the zinc level at Station 7 and all three metal concentrations at Station 9 were less elevated with respect to boundary levels. Chromium results were anomalous in that the mean values for total and dissolved metal were the same at 14.7 µg/L and standard deviations, however, were much greater for total chromium. Chromium levels were also elevated (total, 4.44 µg/L) at Station 5, which represents the auto plant outfall in the lower river.

In Survey 3 (Figures 4.18-4.20, Table 4.12), a similar distribution pattern was seen for the main river stations. In the Monroe WWTP plume (Stations 13-19) zinc levels declined with increasing distance from the outfall, whereas copper and chromium levels increased slightly toward the turning basin. The WWTP was clearly a primary source of zinc. In both Surveys 2 and 3, bottom water at Station 4 appears to be slightly enriched with respect to all three metals.

Survey 4 results (Figures 4.21-4.23, Table 4.13), which included a river plume study in Lake Erie, indicate that chroumium levels generally increased downstream in the river and along the lake shore within the plume. However, lake concentrations at 4-7 µg/L were still far less than those in Station 9 effluent. Copper and zinc levels were also about two-fold higher in general than most river values. Zinc concentrations in Station 7 effluent were still somewhat higher. The zinc concentration at the power plant discharge (Station 29) in Lake Erie was notably higher (33 µg/L) than that in lake water (15 µg/L).

Survey 5 results (Figures 4.24-4.26, Table 4.14) also represent a river plume gradient in Lake Erie, originating largely at Station 29 (power plant outfall). The dilution gradient is most apparent for total and

dissolved copper (Figure 4.25). Station 7 was, again, a dominant source of high zinc concentrations (32 μg/L).

In Surveys 6-10 (Figures 4.27-4.41, Tables 4.15-4.19) only four stations were sampled for metals: Stations 1, 4 and 26 in the river, and Station 29 near the power plant outfall. Its intake in the river was near Station 5, the auto plant outfall. In all of these surveys, copper concentrations were notably elevated 2 to 3-fold at Station 29 relative to levels at the river stations. In general, zinc concentrations at Station 4 (turning basin) were not markedly higher than at Station 1 despite zinc loadings from Station 7 (WWTP) between them. In most cases, chromium levels were slightly higher at Station 4 than at Station 1.

4.5 TEMPORAL PROFILES, METALS

Temporal profiles for all surveys (1-10) at Station 1 (Figures 4.42-4.44) indicate that average concentrations of all three metals (except possibly zinc) were not very different in the fall (1983) and spring (1984). However, variability was greatly increased under high flow conditions in the spring. Average zinc levels appear to have been somewhat higher in the spring.

Temporal profiles for Station 4 (Figures 4.45-4.47) indicate a more constant variability for concentrations of all three metals in the fall and spring. In general, copper and chromium concentrations were similar at Stations 1 and 4 throughout the year. Zinc concentrations approximately 2-fold higher at Station 4.

A summary of metals data from selected stations for all 10 surveys is shown in Table 4.20.

4.6 METALS QC

In the case of metals, the results of bottle, filter, and digestion blanks analysis are already subtracted from the sample data presented here.

Detection limits for all three metals analyzed are given in Table 3.1.

Table 3.2 shows that no correction was required for the filtering process in any of the surveys. Furthermore, since the batch blanks were below the detection limits for all metals, bottle blanks were assumed to be negligible for all surveys. Only filter blanks were collected in Survey 2. These blanks were below the detection limit and, therefore, were considered negligible.

Results of several intercomparison studies are presented in Table 3.3. The LLRS results (actual) were compared with the QC sample data from EPA, Cincinnati, represented by the "true values". The $\bar{x}$ is their mean recovery. The 95% confidence level is their mean recovery $\pm$ two standard deviations. In both of these series, the LLRS results fell within the 95% confidence interval (mean recovery $\pm$ two standard deviations).

No chemical interferences were found when analyzing copper and zinc, as indicated by the recovery data (Table 3.4). The concentrations were calculated directly from a linear regression of synthetically prepared standard solutions. However, the analyses still included a standard addition determination on every fifth sample in order to monitor recovery throughout the study. Recovery here was defined as the slope of the standard addition calculation for a sample x 100, divided by the mean slope of the standard addition for the standard.

In contrast, the mean recovery for dissolved and total chromium was well above 100% (Table 3.4). This indicates interferences were present

which enhanced the analytical signal and, therefore, standard additions was used to determine the concentration of this metal. There was no need to correct the reported chromium data to reflect this enhancement. This was accomplished by calculating the concentration of each sample using the method of standard additions.

Every tenth sample collected in the field included a duplicate, which was processed in the same way as any other sample collected. The standard deviation calculated for samples and their duplicates gives an estimate of the overall precision, including both field and instrumental variations (Table 3.5).

The following equation was used to calculate the standard deviation:

$$\text{Standard deviation} = \sqrt{\frac{\Sigma d^2}{k}}$$

where, d = difference between the sample and its duplicate.

k = number of duplicates.

Ideally, the standard deviation for a set of samples and duplicates should be the same. Three sample-duplicate data sets were created for water samples: river, lake, and the Monroe Wastewater Treatment Plant. Table 5 shows the results. Differences between duplicates collected during a storm event on Lake Erie during Survey IV (Table 3.6) seems to suggest that the storm had a rather large impact on the overall variability in the samples collected during this cruise. These samples were not included with other Lake Erie samples because of their probable different standard deviation due to the high solids concentrations in these samples.

Certain samples were analyzed once a day for a number of days as "between-run" replicates. The observed variability of these replicates (Table 3.7) was assumed to be due to laboratory and instrumental procedures

only. The field duplicates mentioned earlier were potentially more variable since there was additional uncertain related to field conditions; i.e., bottle blanks, filtering and possible non-homogenity of the water samples. The standard deviations in Table 3.5 do not appear to be much higher than the standard deviations in Table 3.7. This suggests that the variability of our reported results for copper, zinc, and chromium was mainly due to laboratory and instrumental procedures.

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APPENDIX

RIVER RAISIN FLOW DATA DURING SURVEYS 1-10

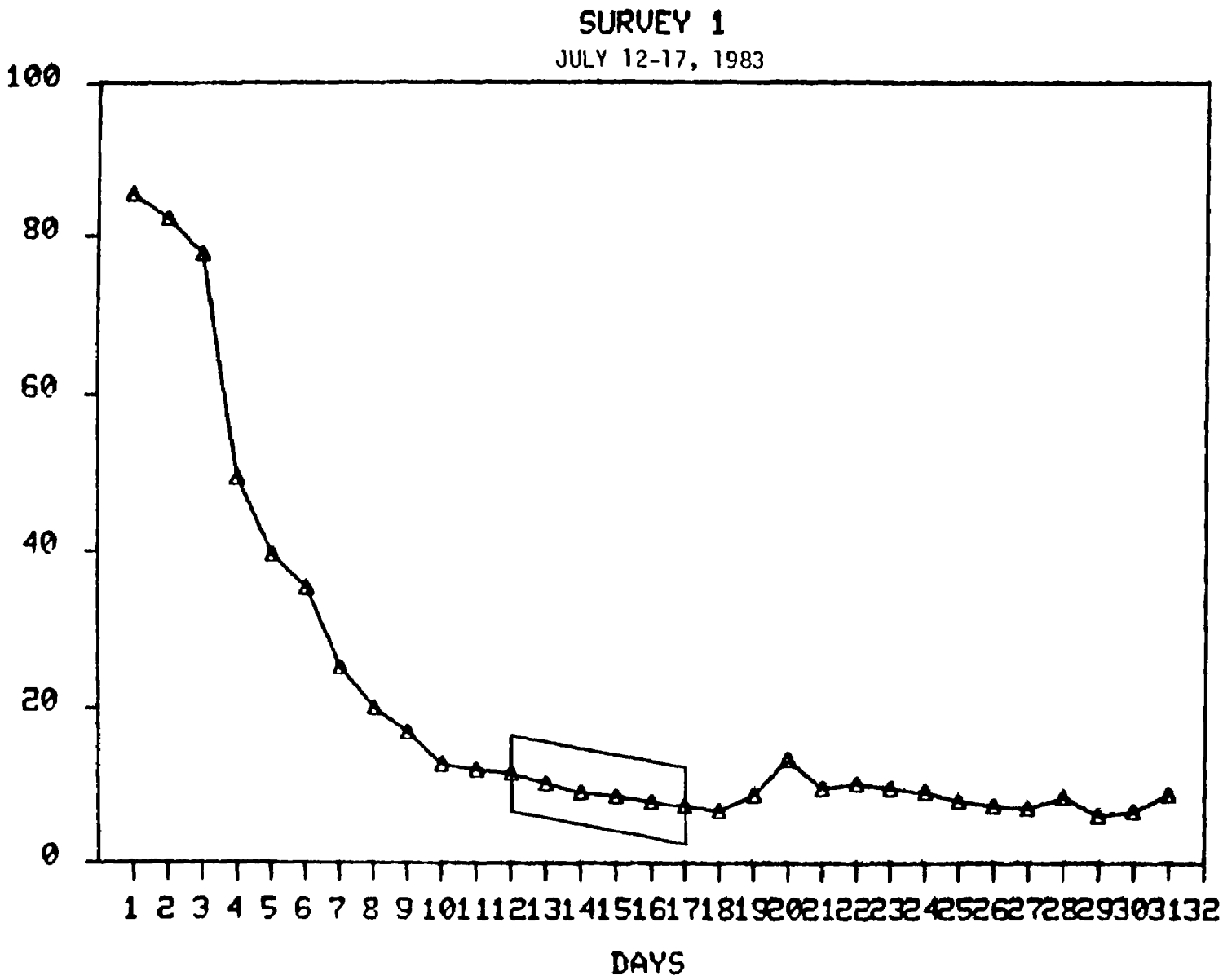


Figure A.1. River Raisin flows at Monroe during Survey 1.

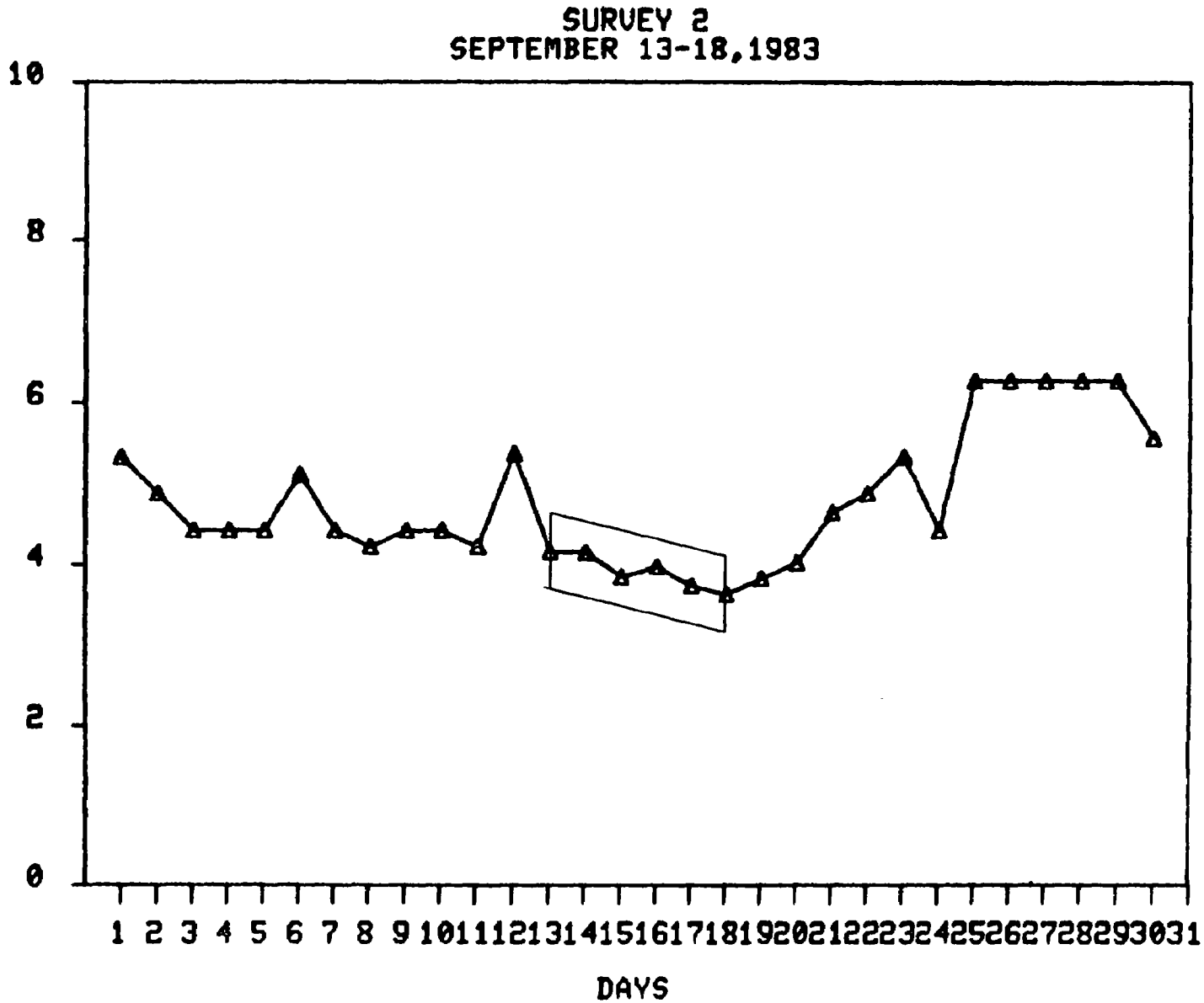


Figure A.2. River Raisin flows at Monroe during Survey 2.

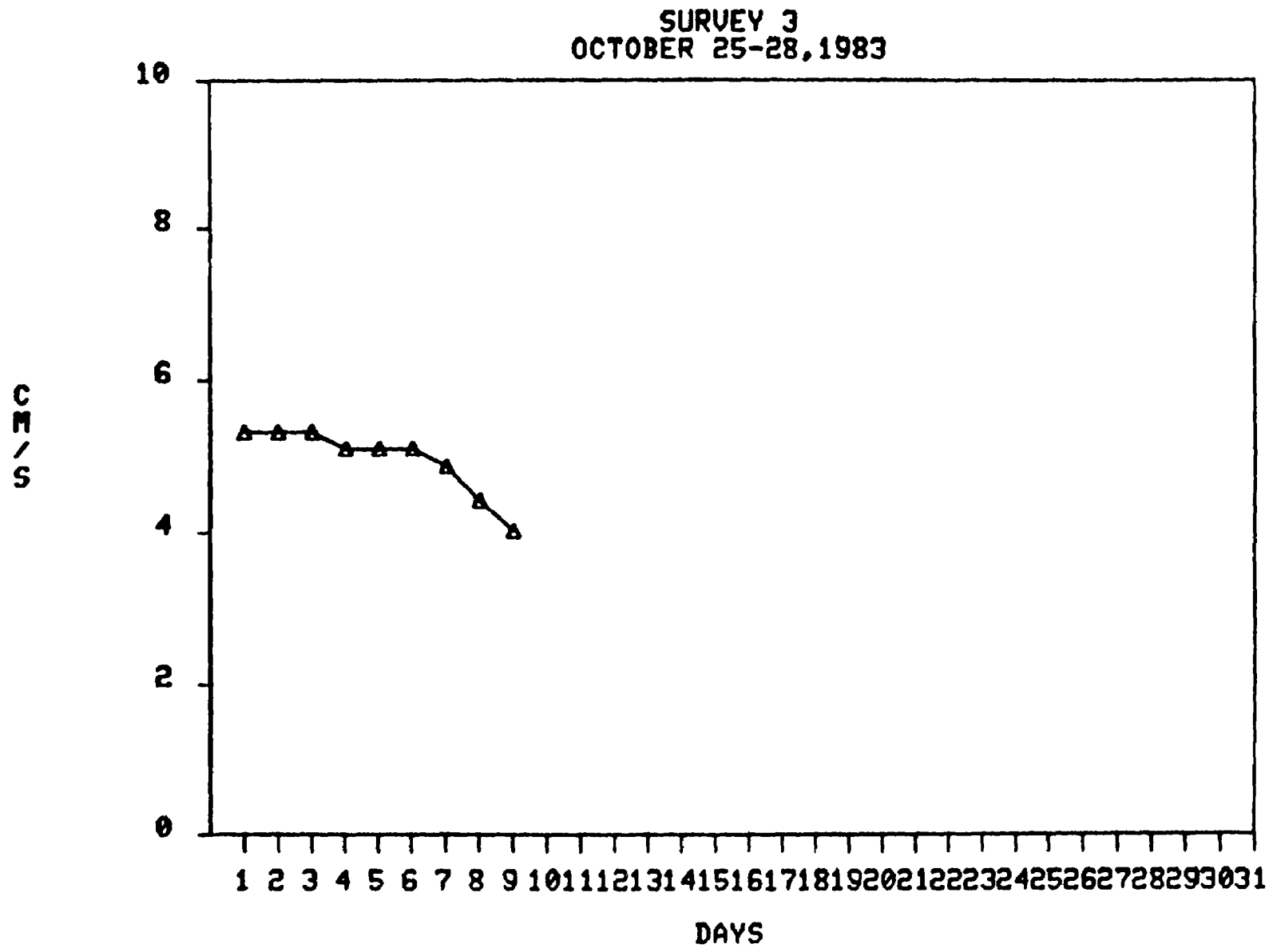


Figure A.3. River Raisin flows at Monroe during Survey 3.

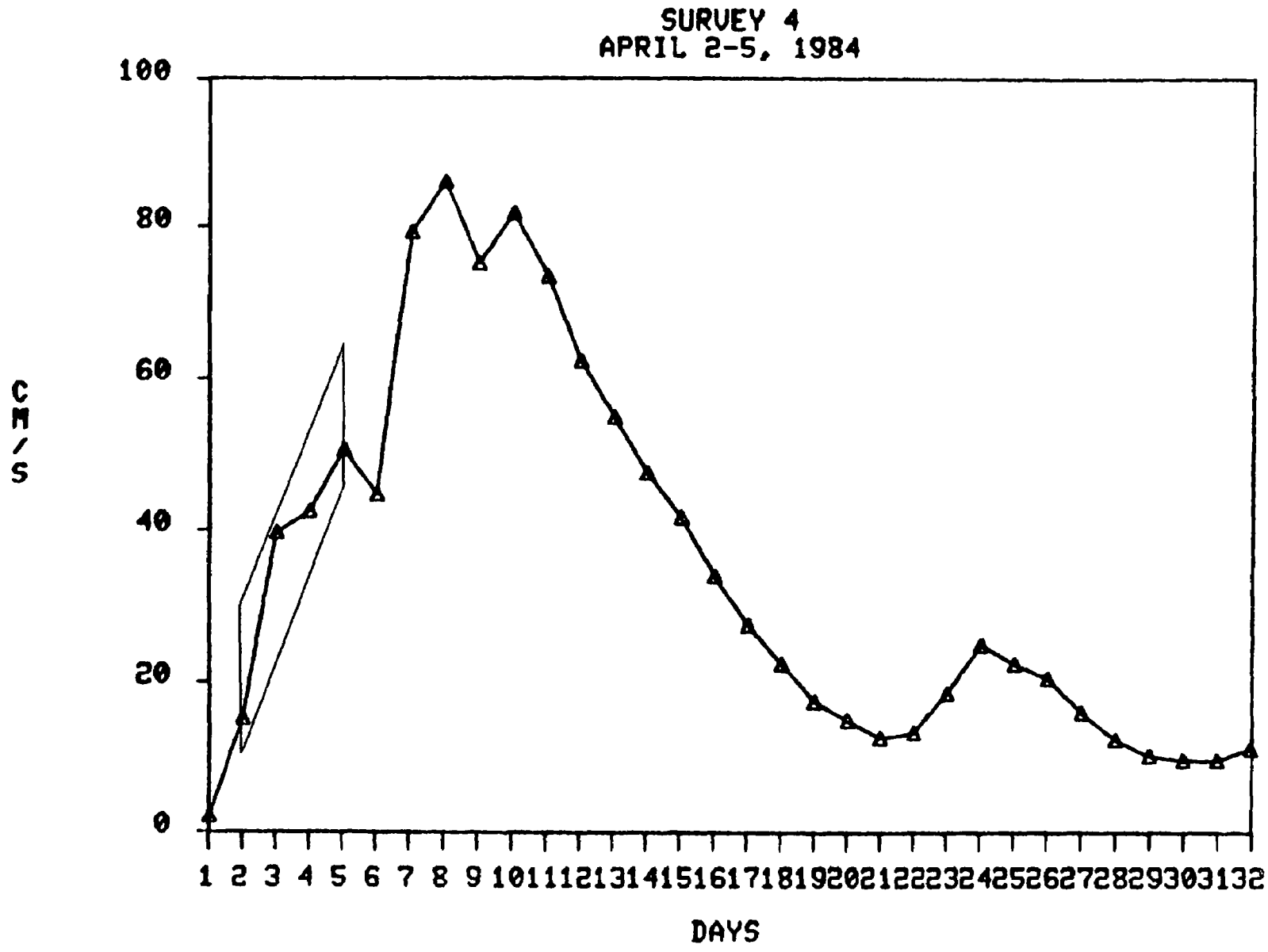


Figure A.4. River Raisin flows at Monroe during Survey 4.

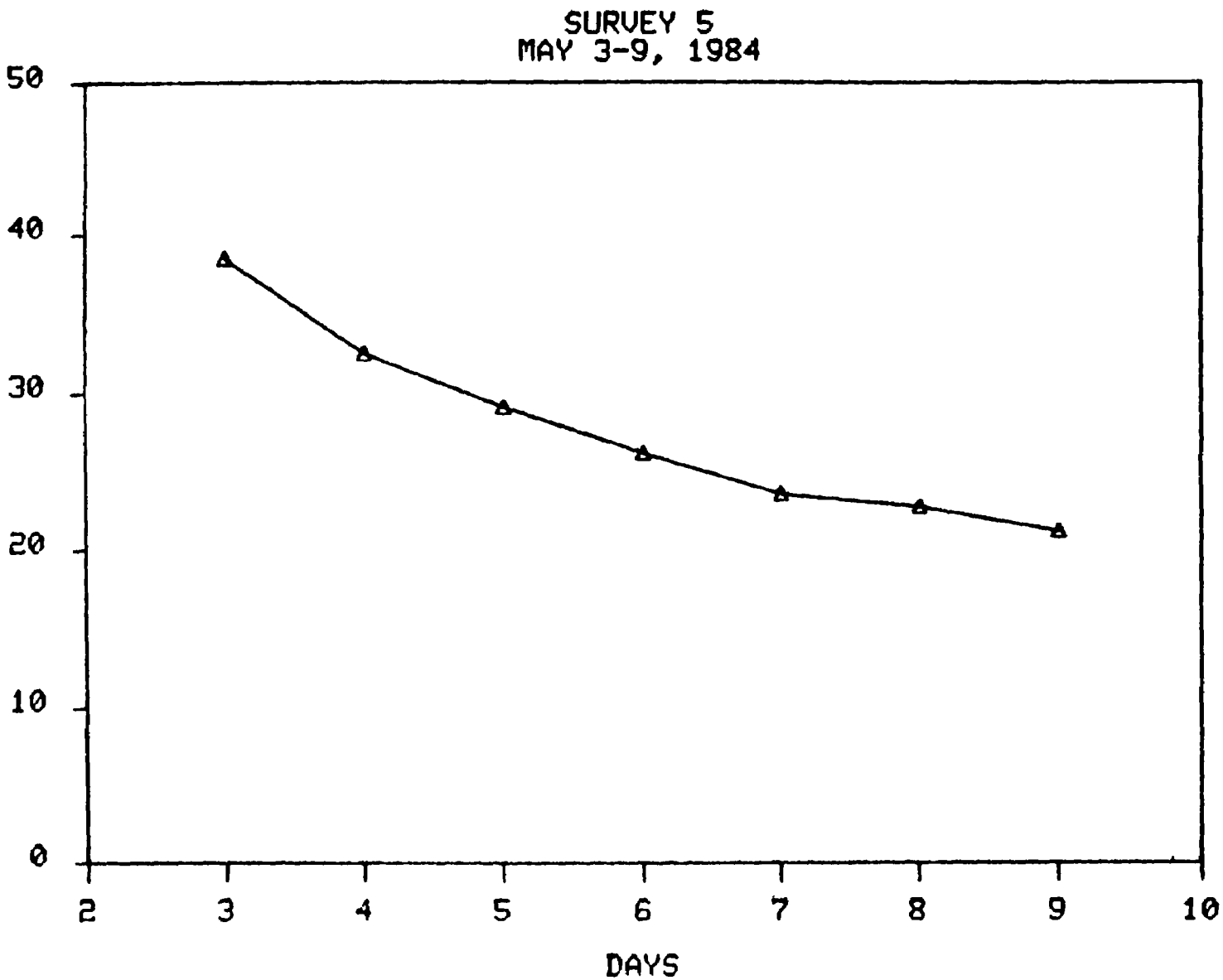


Figure A.5. River Raisin flows at Monroe during Survey 5.

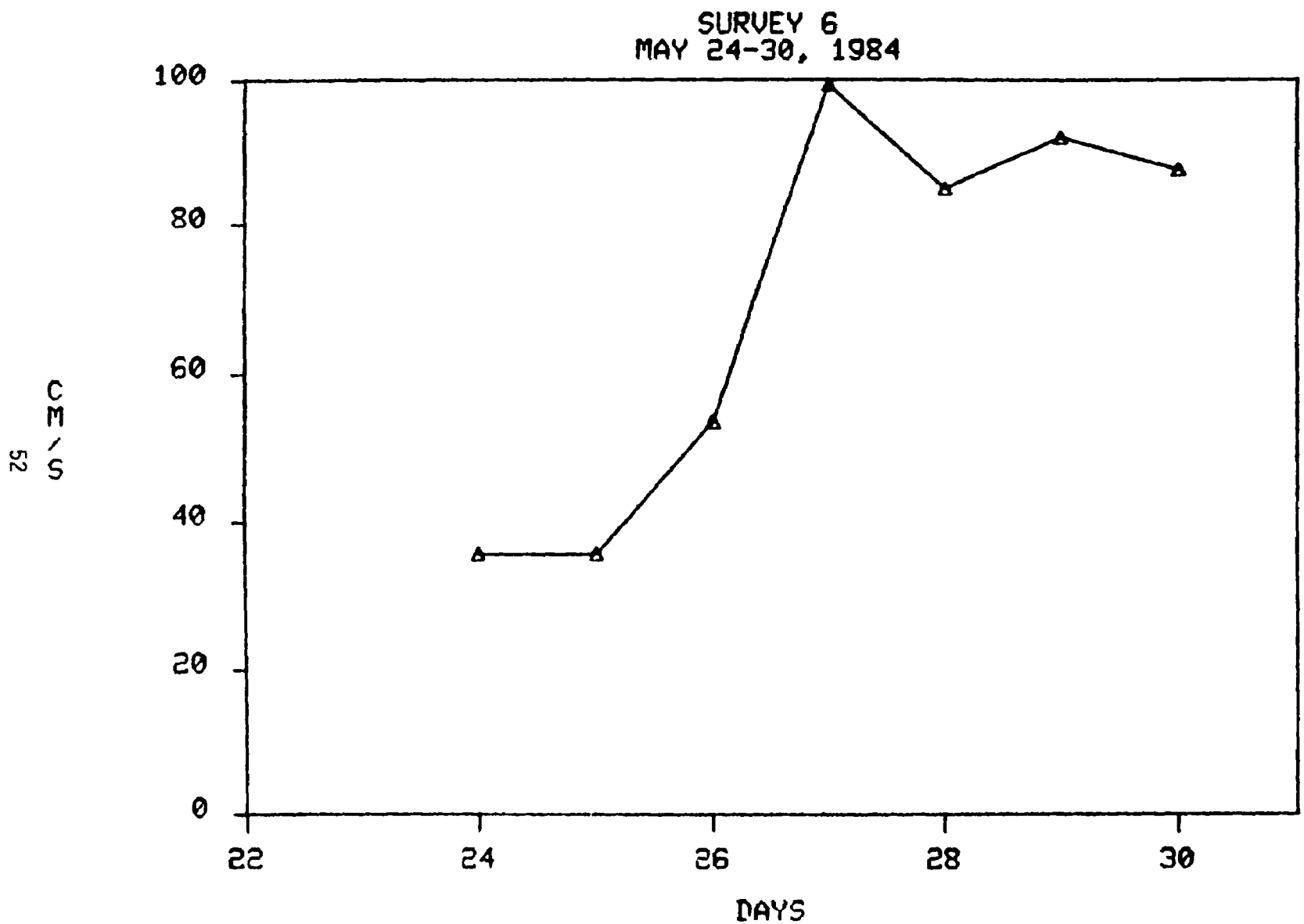


Figure A.6. River Raisin flows at Monroe during Survey 6.

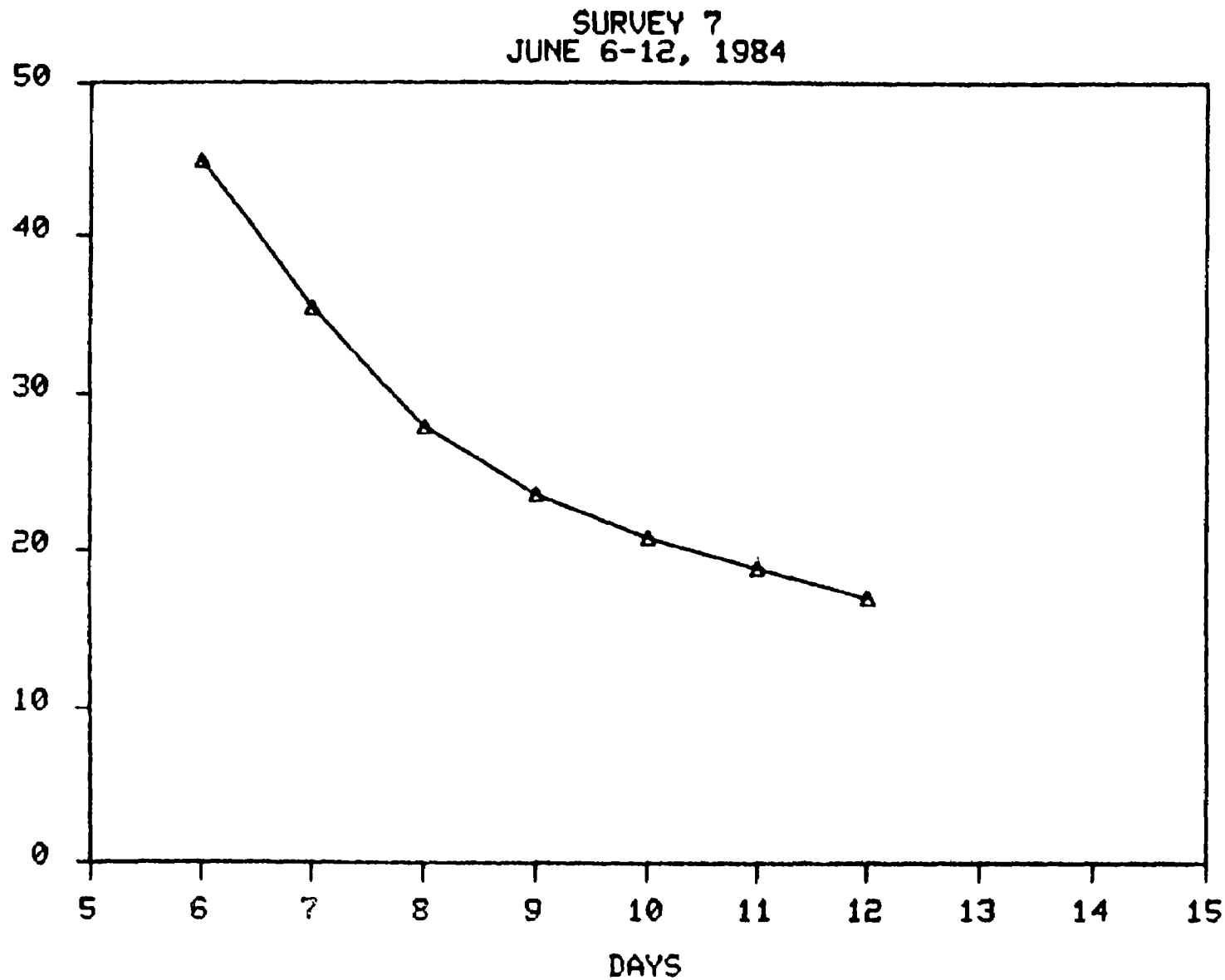


Figure A.7. River Raisin flows at Monroe during Survey 7.

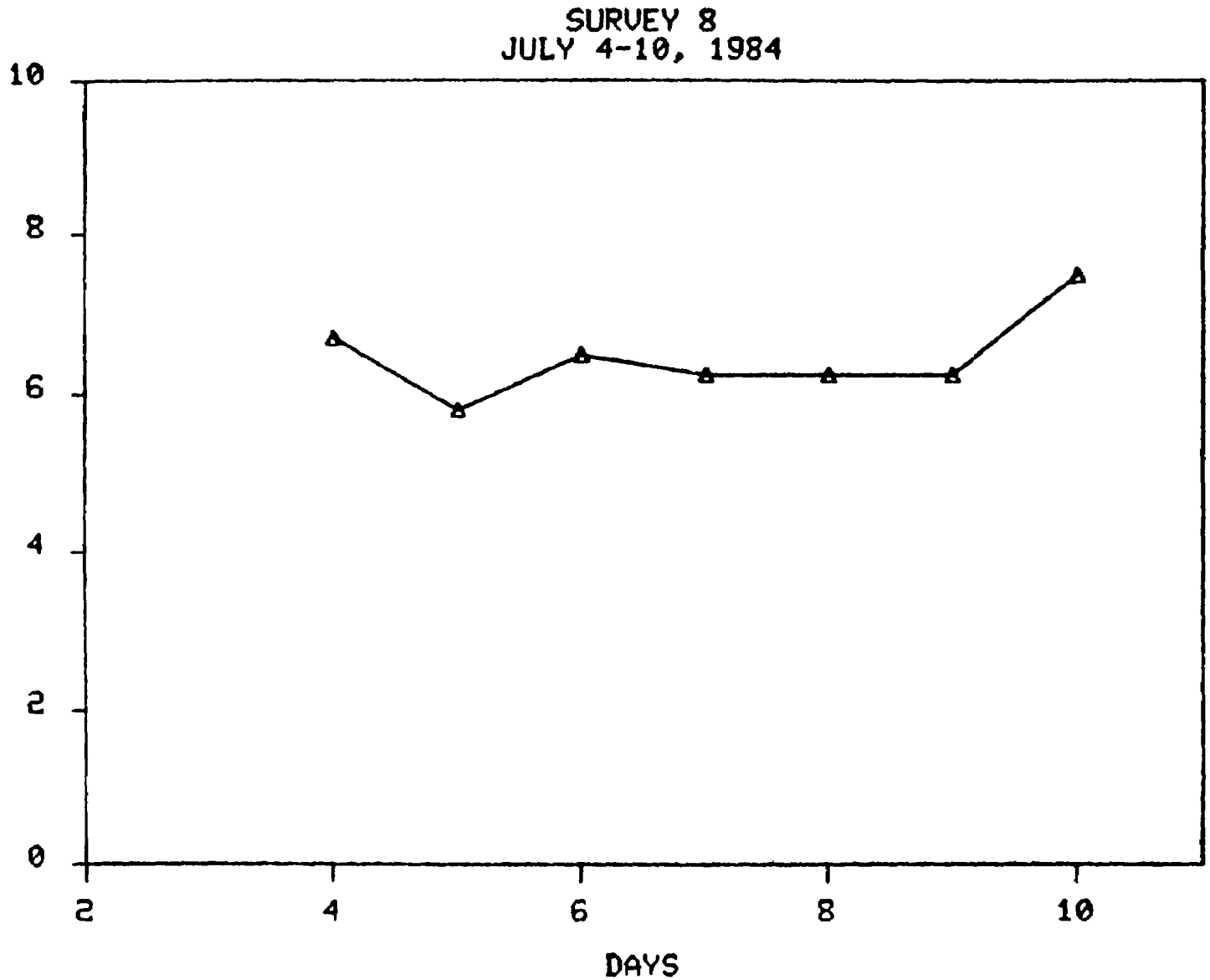


Figure A.8. River Raisin flows at Monroe during Survey 8.

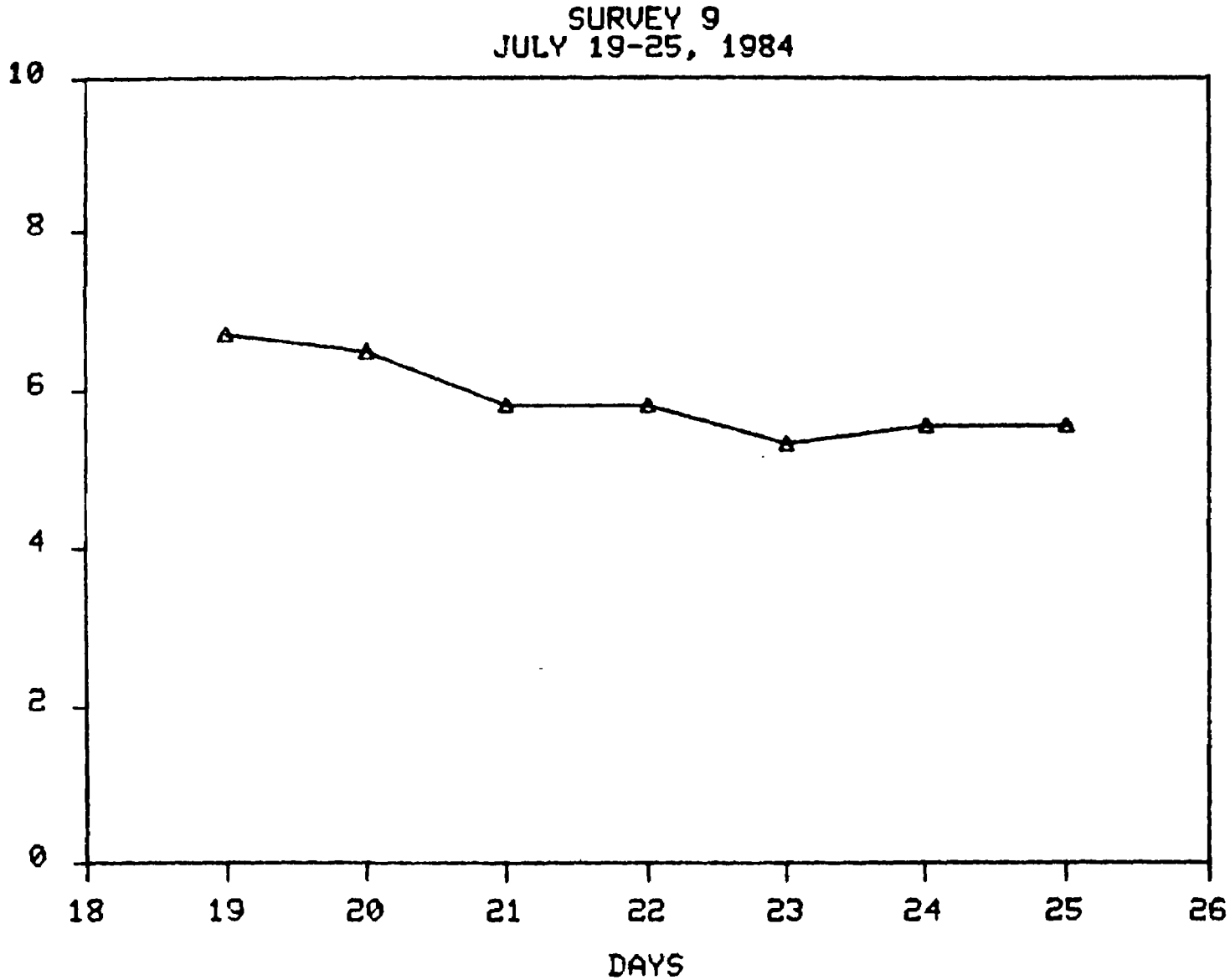


Figure A.9. River Raisin flows at Monroe during Survey 9.

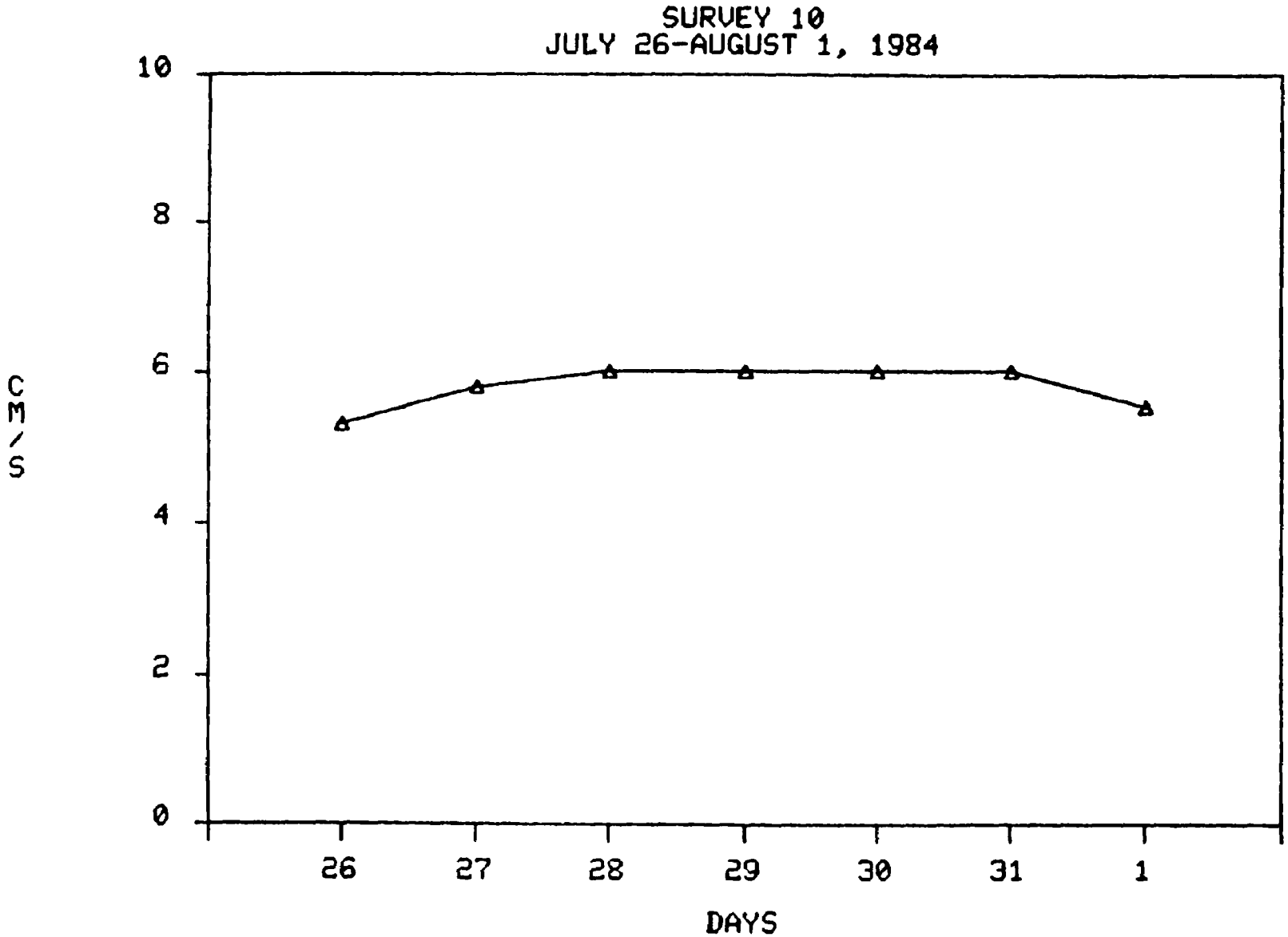


Figure A.10. River Raisin flows at Monroe during Survey 10.

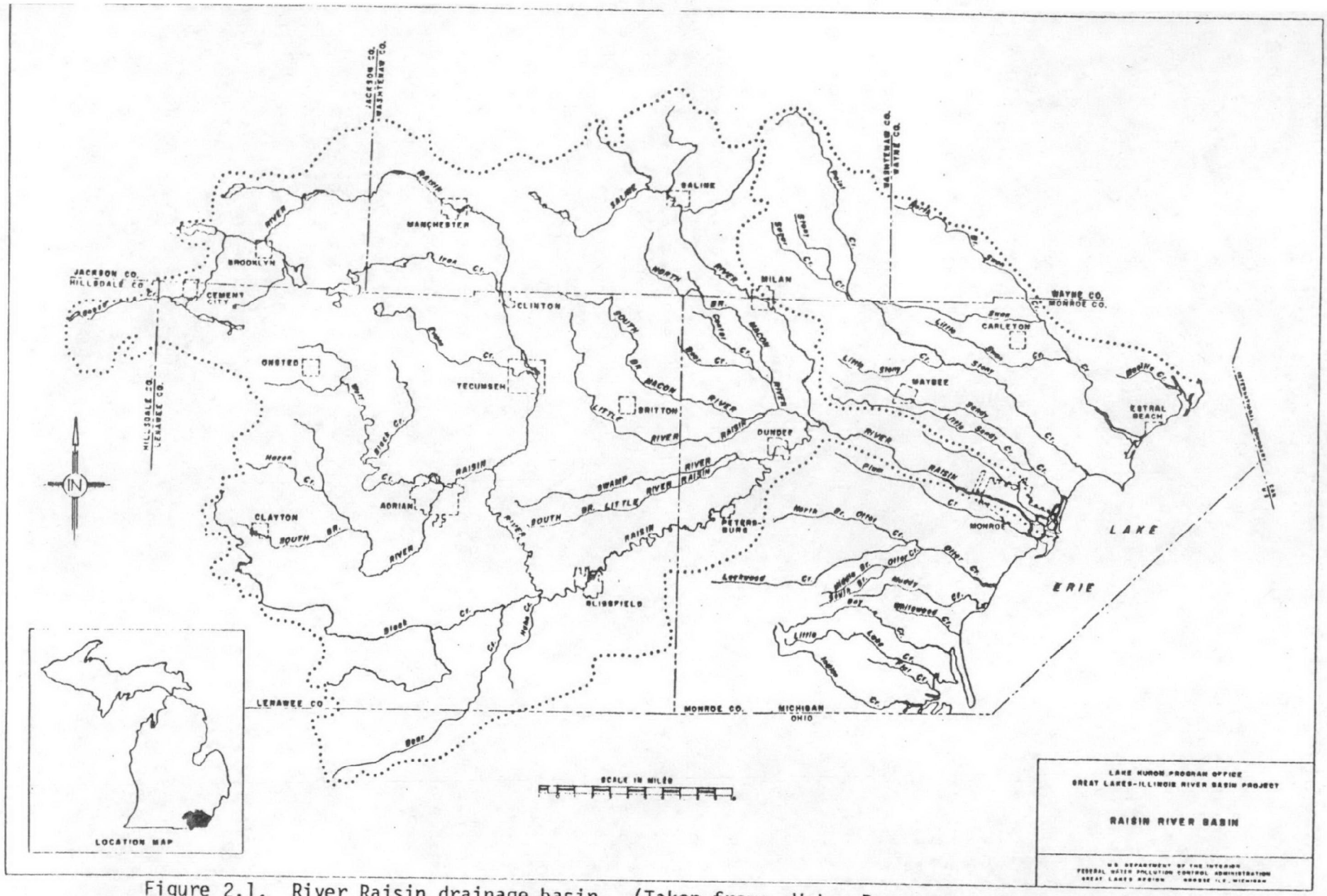


Figure 2.1. River Raisin drainage basin. (Taken from: Water Resources - Conditions and Uses - In the River Raisin Basin; Michigan Water Resources Commission, 1965.)

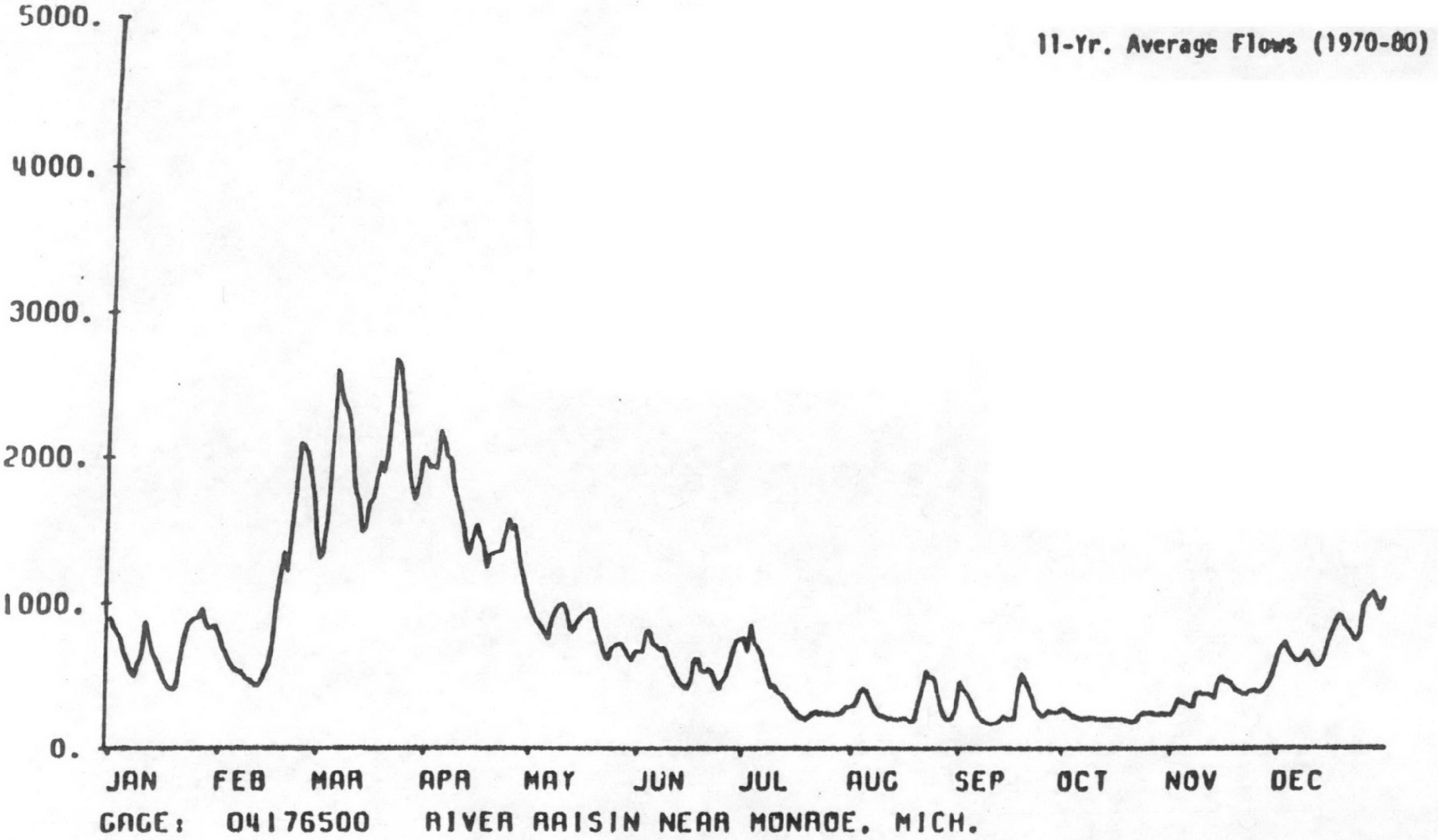


Figure 2.2. Raisin River 11-year average daily flow (cfs) 12 km upstream from Lake Erie (USGS data).

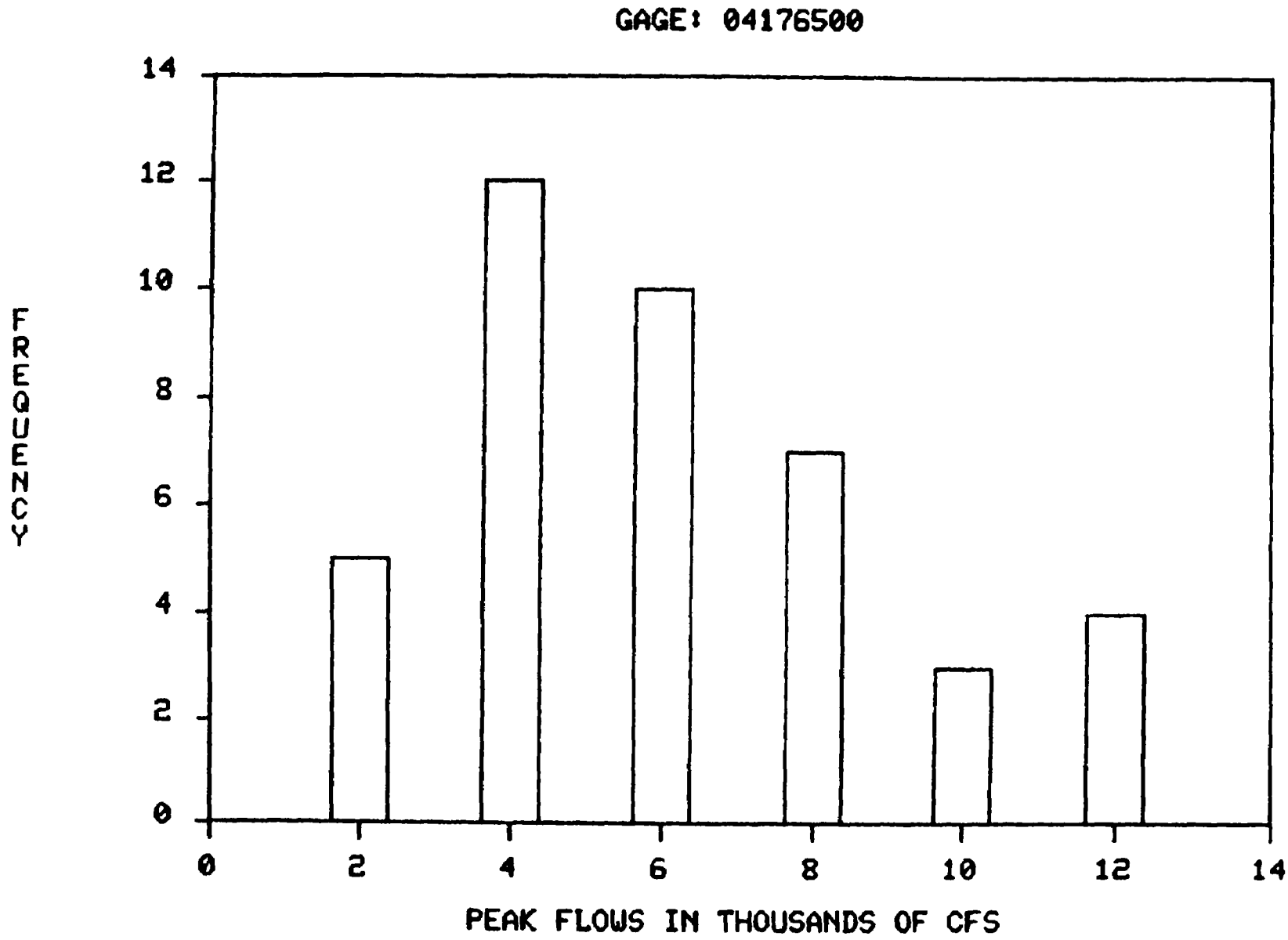


Figure 2.3. Peak flows in the River Raisin at Monroe since 1938.
(Data from the U.S.G.S.)

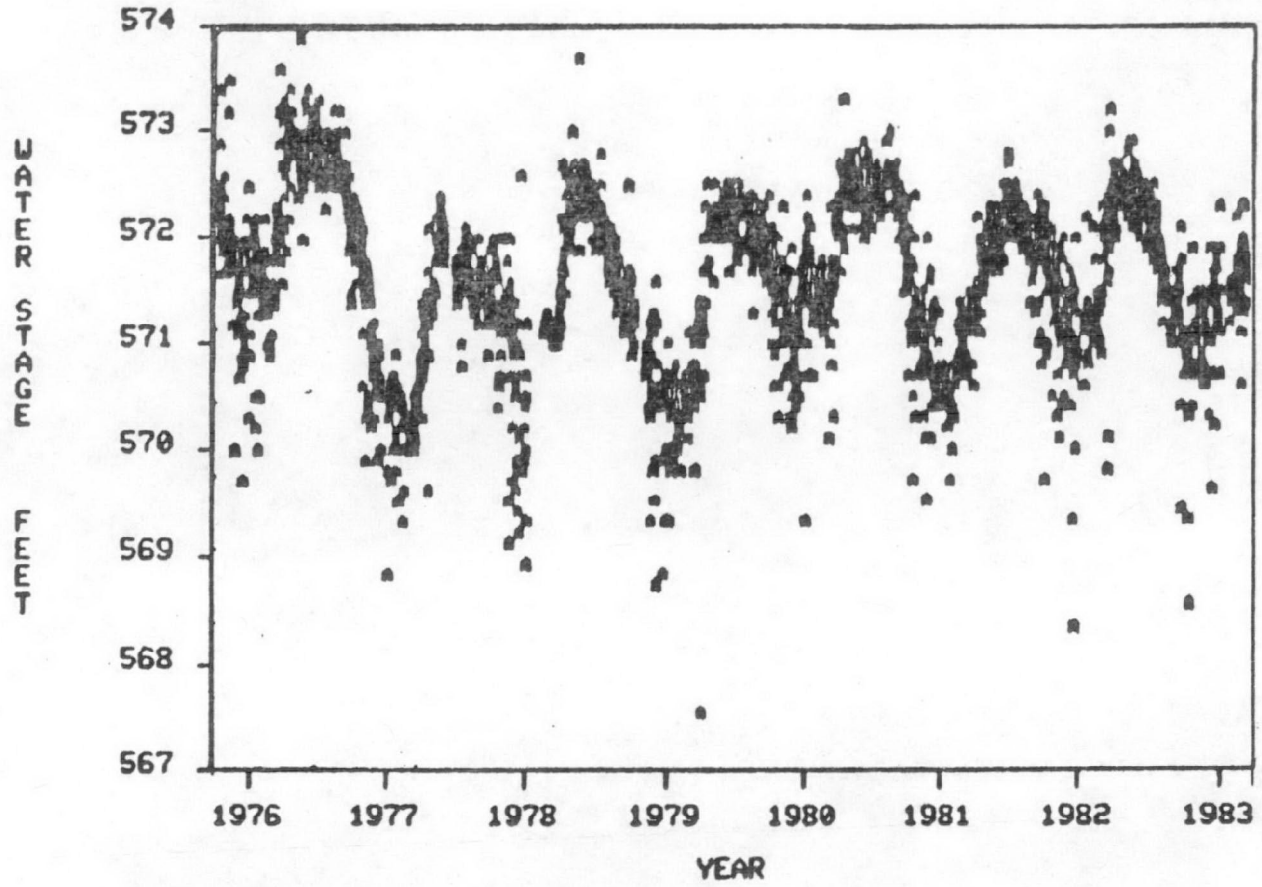


Figure 2.4. Lake Erie level at gage 3087. Data is from NOAA.

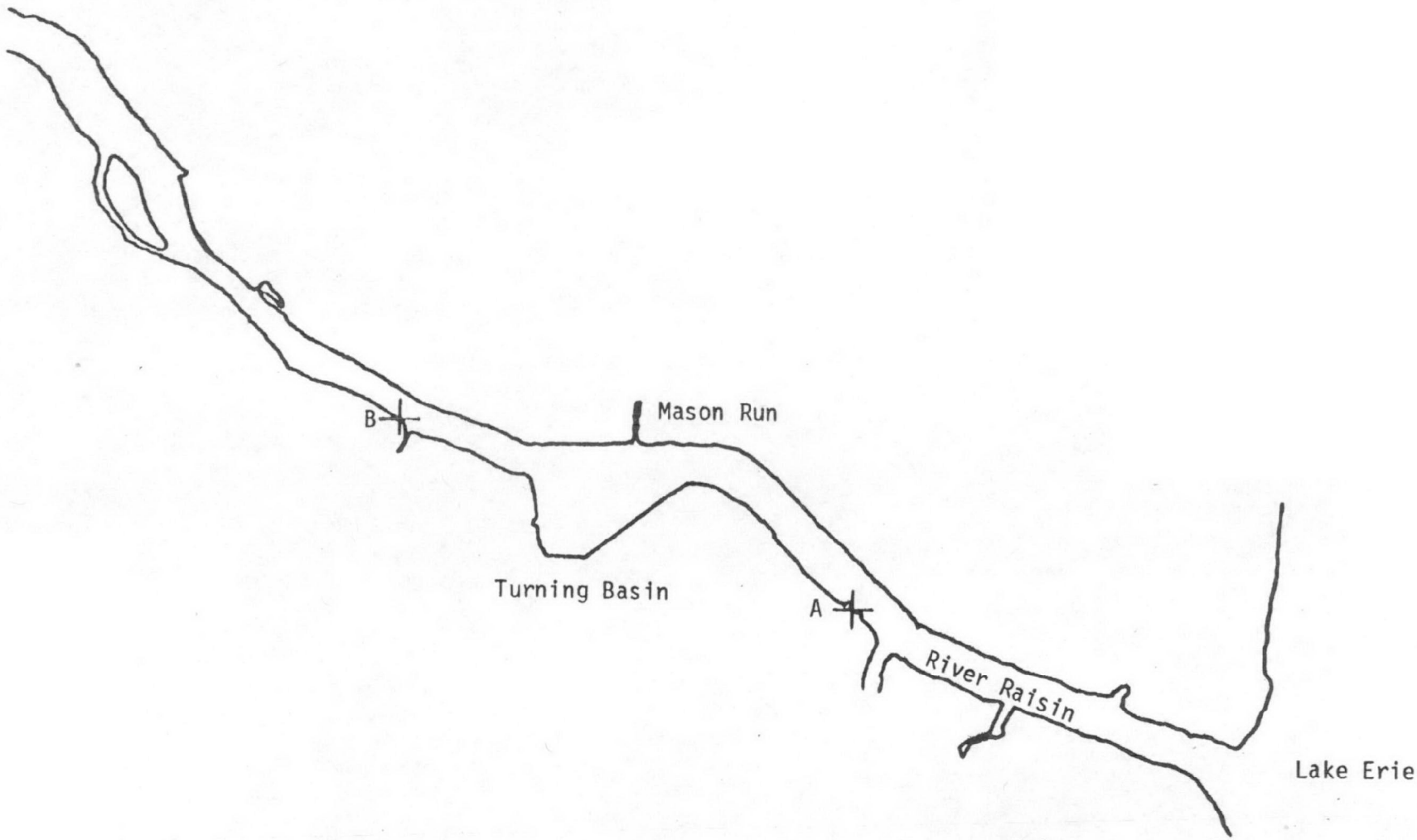


Figure 2.5. The Monroe Harbor Study Area. Points A and B are reference points for the depth profile map in Figure 6.

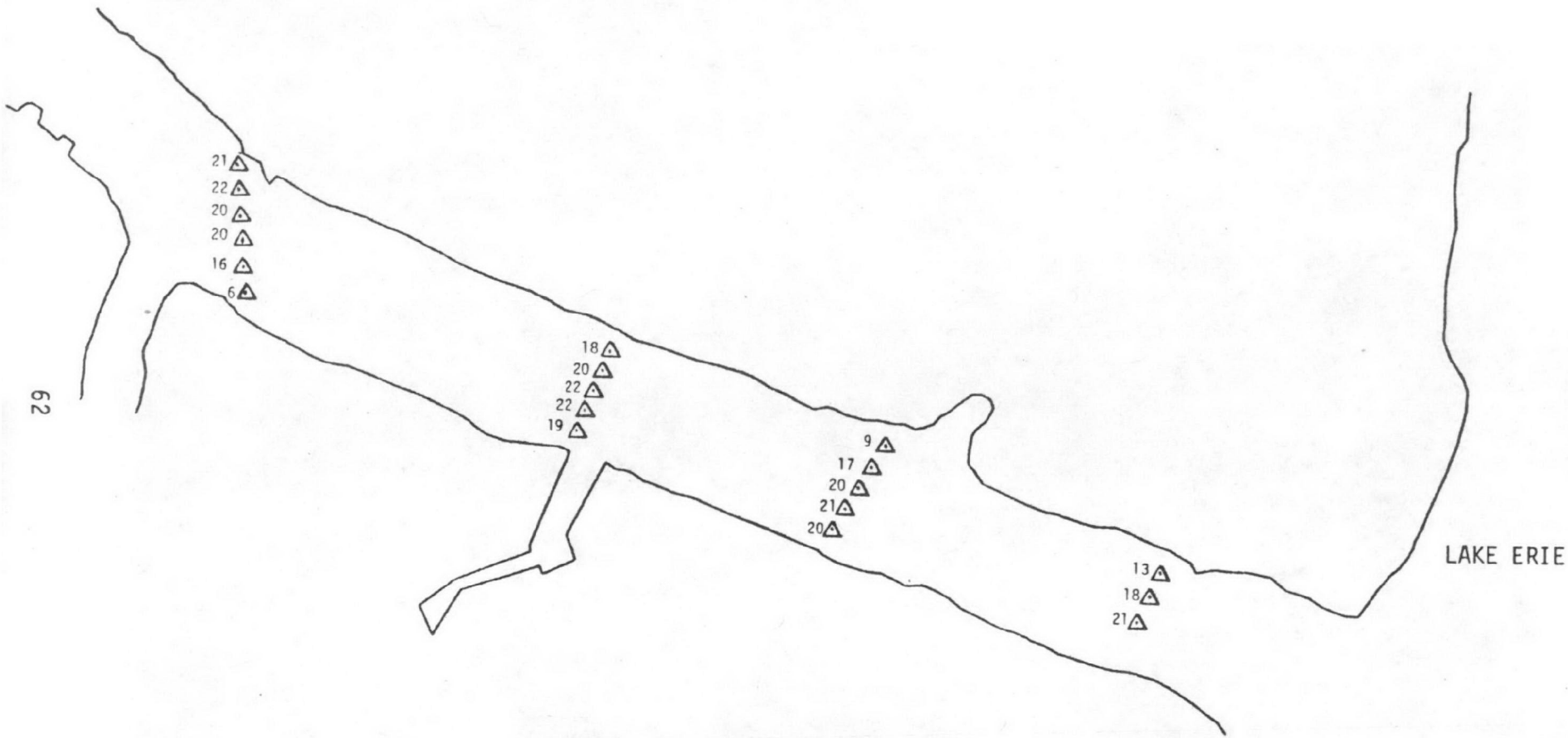


Figure 2.6. River Raisin depth profiles (feet). Depths are referred to International Great Lakes Datum (1955) for Lake Erie elevation 568.6 ft. above mean water level at Father Point, Quebec. Data from Computer Sciences Corporation at the EPA Large Lakes Research Station, August 7, 1984.

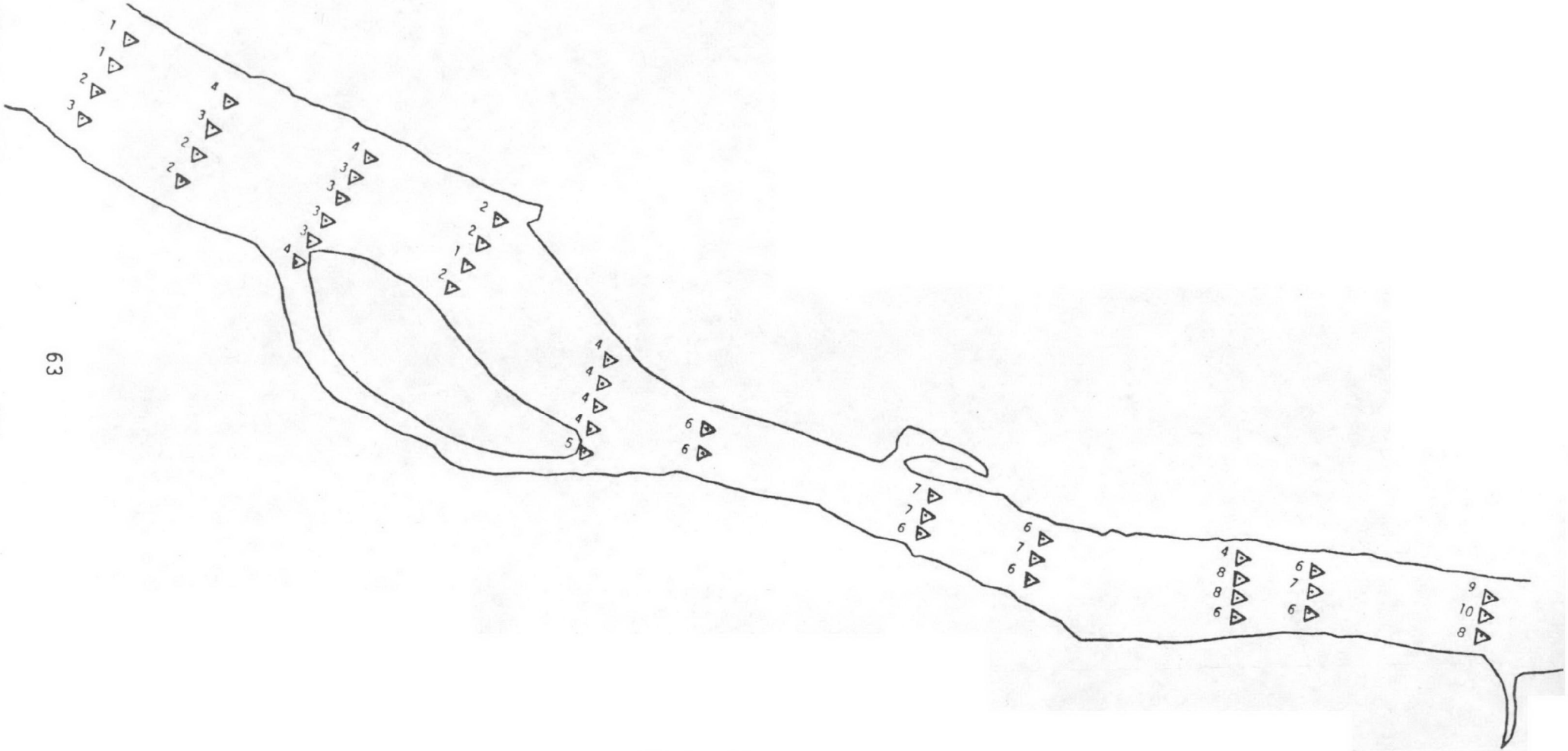


Figure 2.6 (Cont'd.)

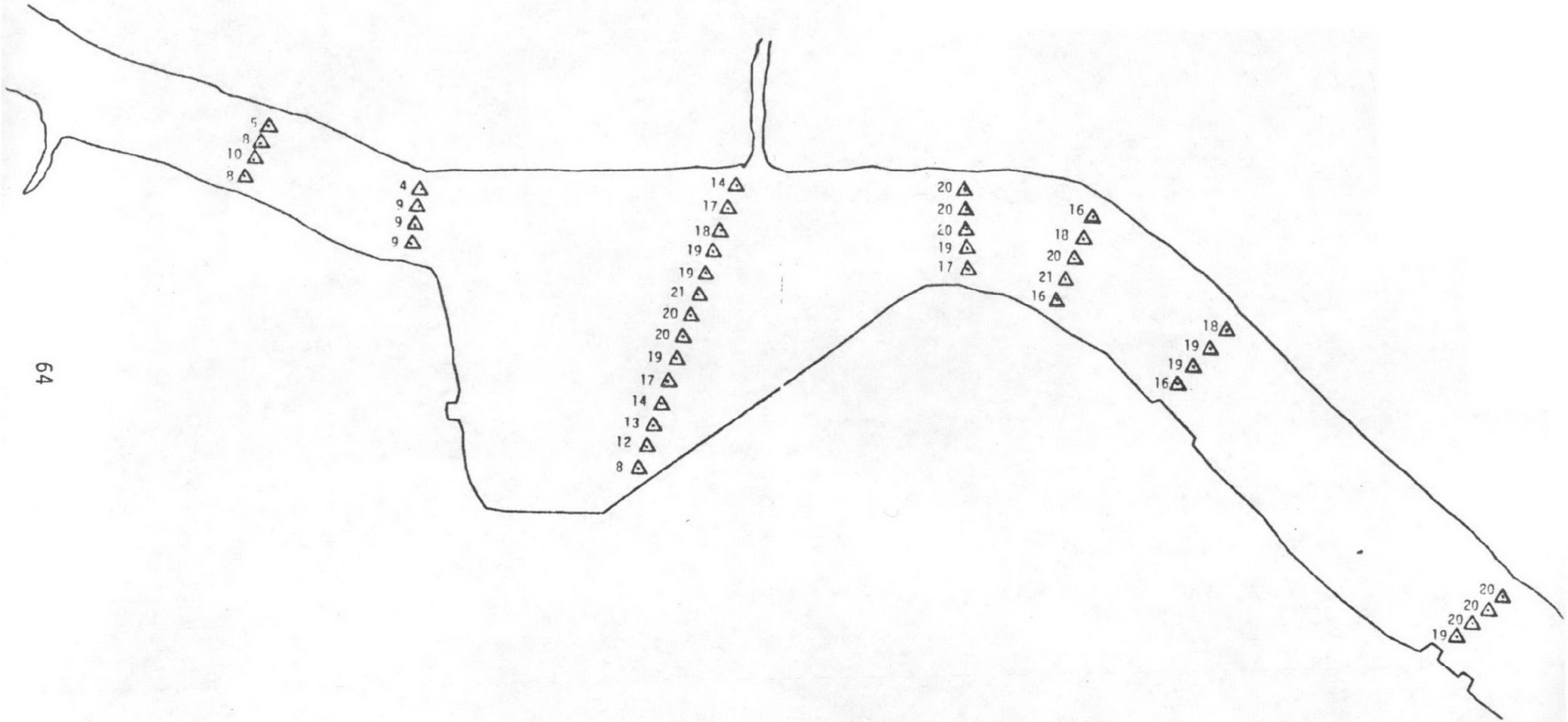


Figure 2.6 (Cont'd.)

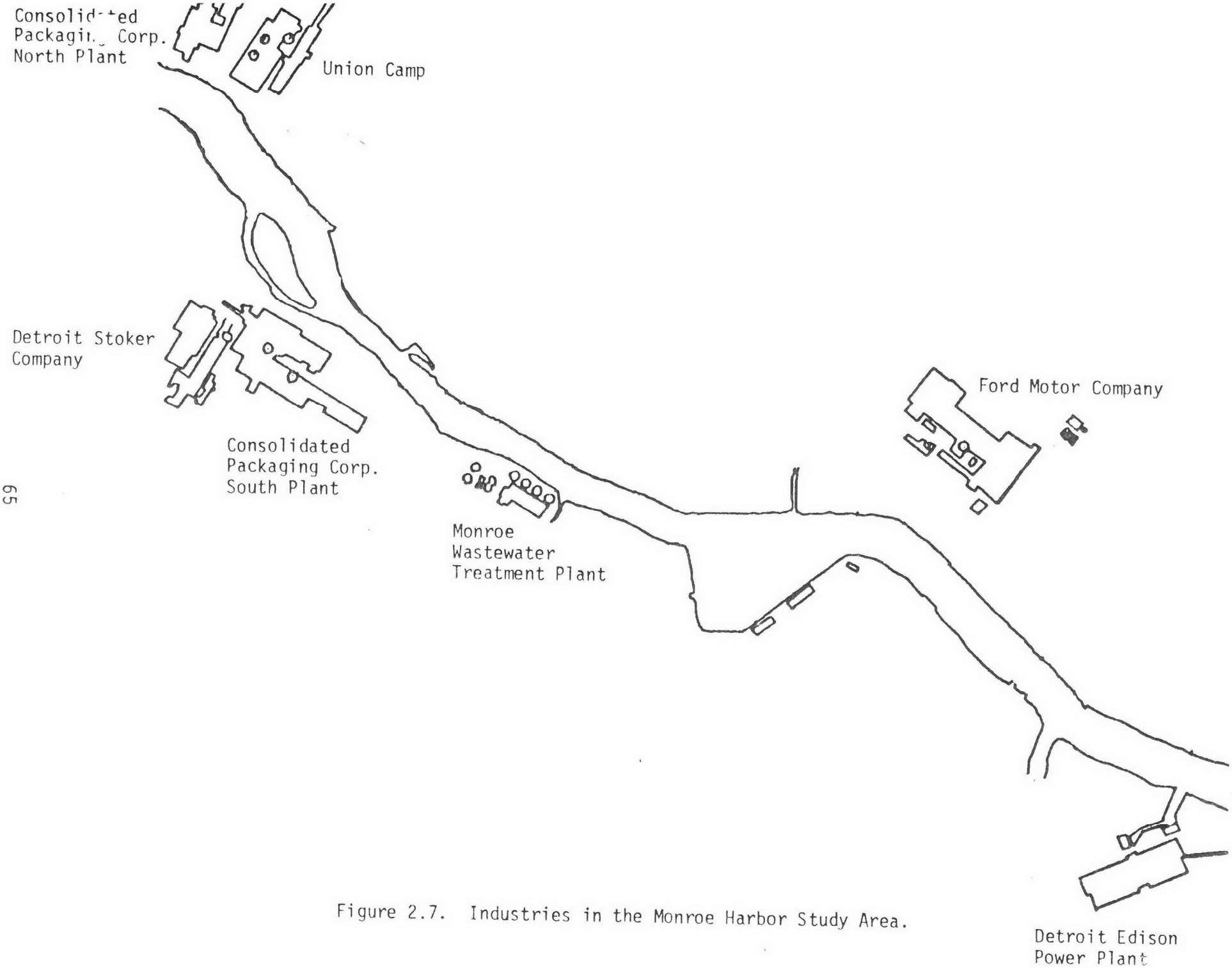


Figure 2.7. Industries in the Monroe Harbor Study Area.

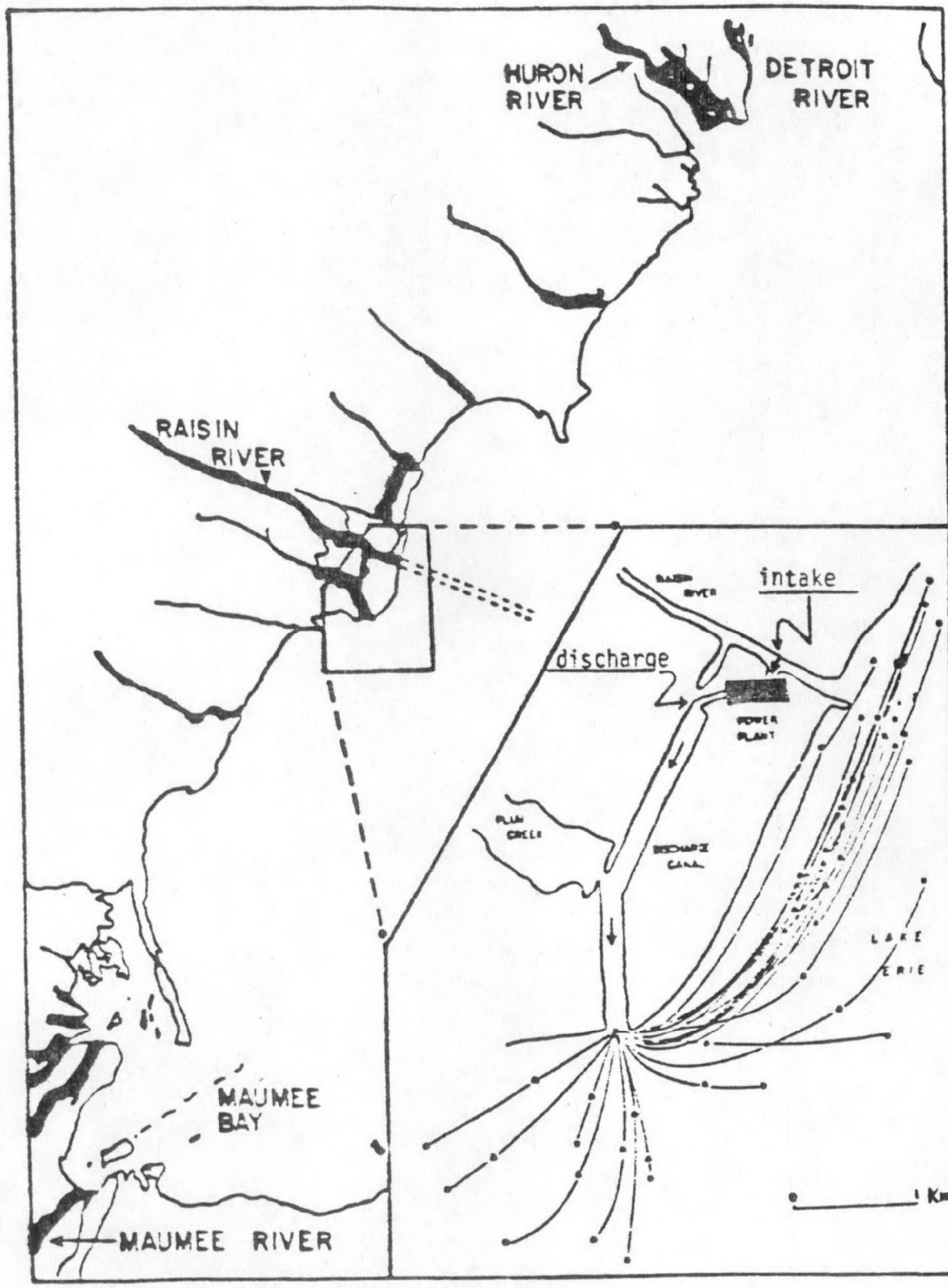


Figure 2.8. The Monroe Power Plant cooling intake and discharge. Also shown are results of a heated effluent plume study. (Cole, 1978).

Fig. 3.1. Stations sampled during Monroe Harbor Survey 1 (July 12-17, 1983).

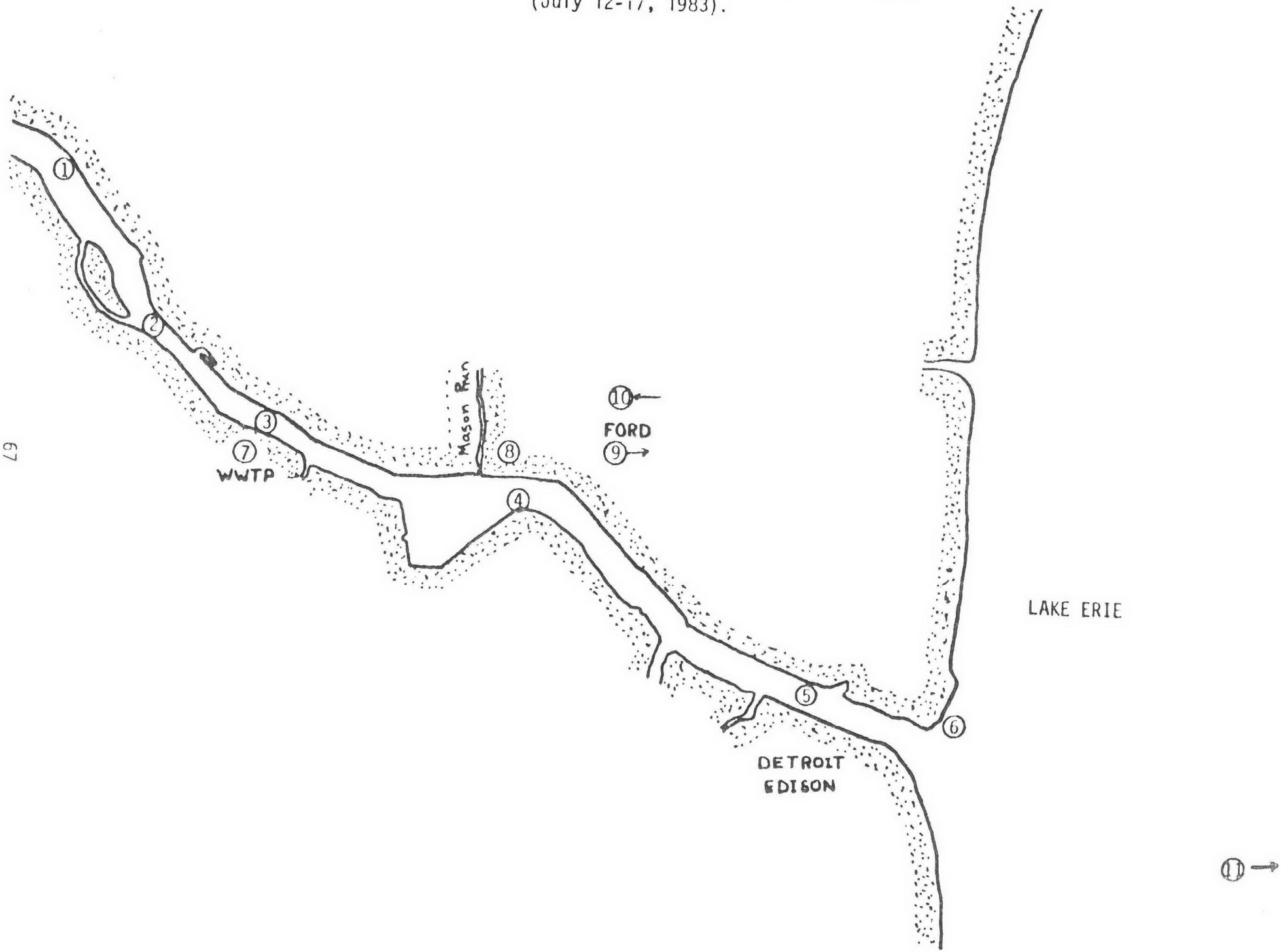


Fig. 3.2. Stations sampled during Monroe Harbor Survey 2 (September 15-18, 1983).

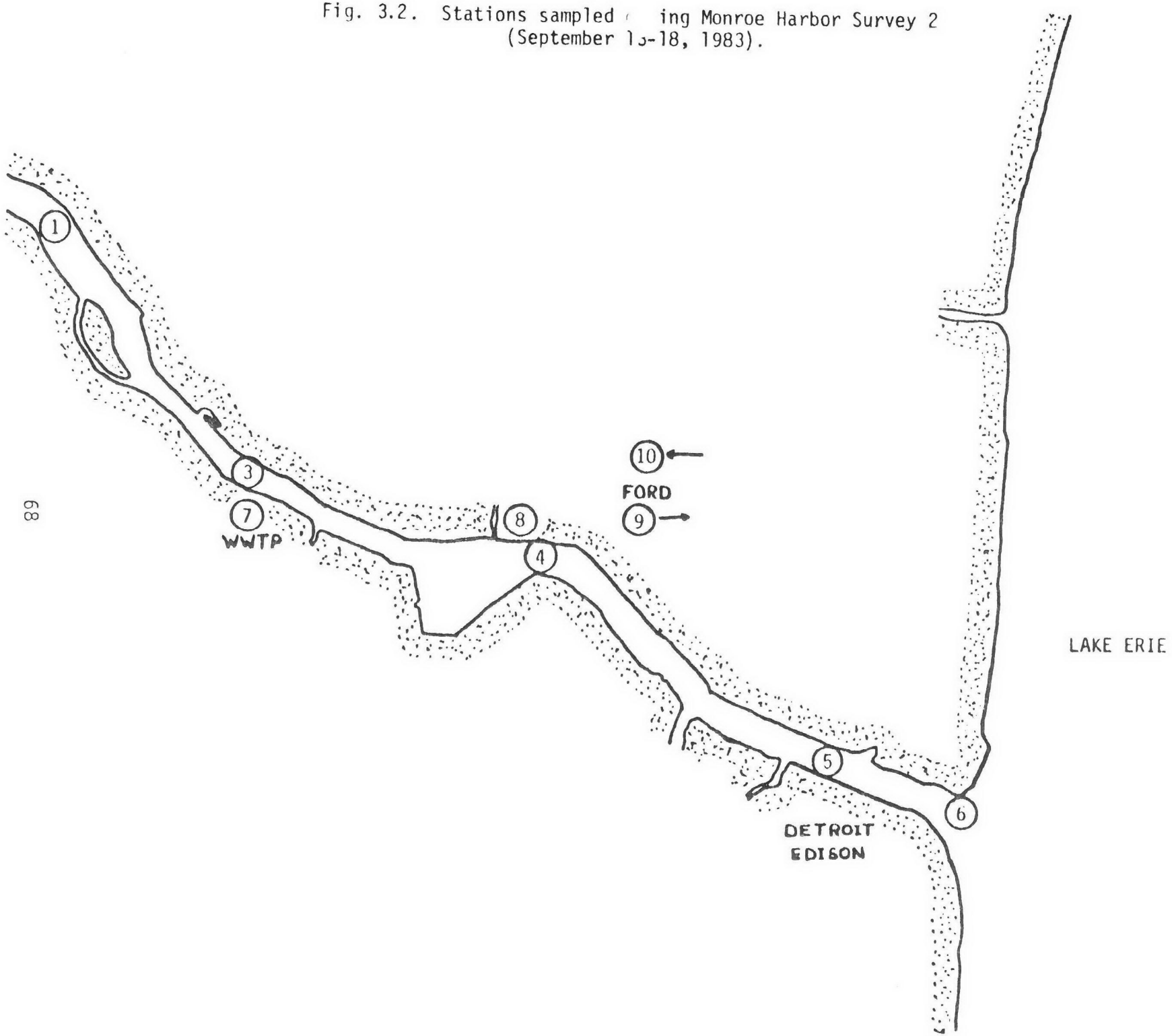


Fig. 3.3. Stations sampled during Monroe Harbor Survey 3 (October 25 - November , 1983), including the Waste Water Treatment Plume.

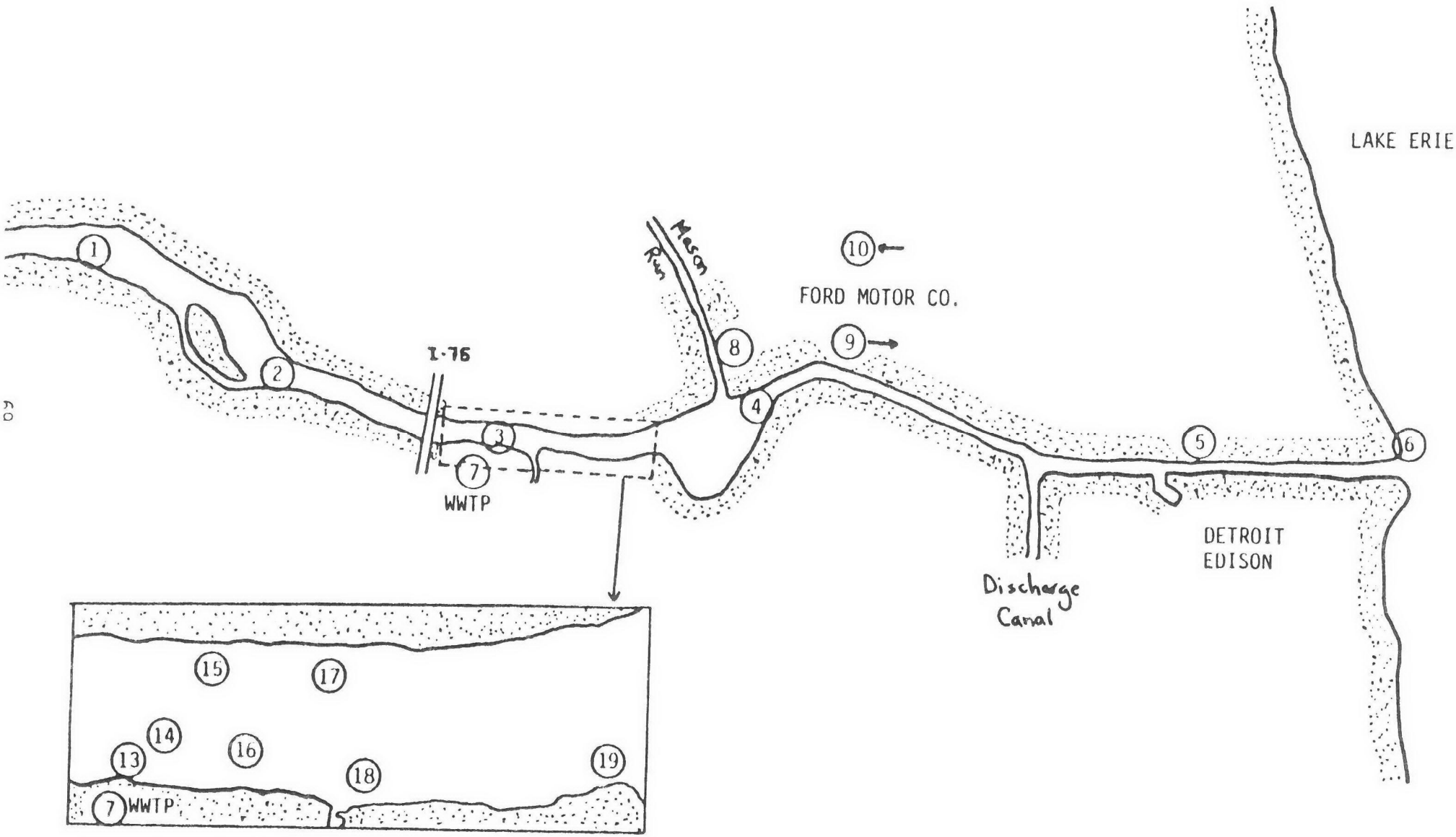


Fig. 3.4a. Stations sample during Monroe Harbor Survey 4 (April 2-5, 19[illegible]): River stations.

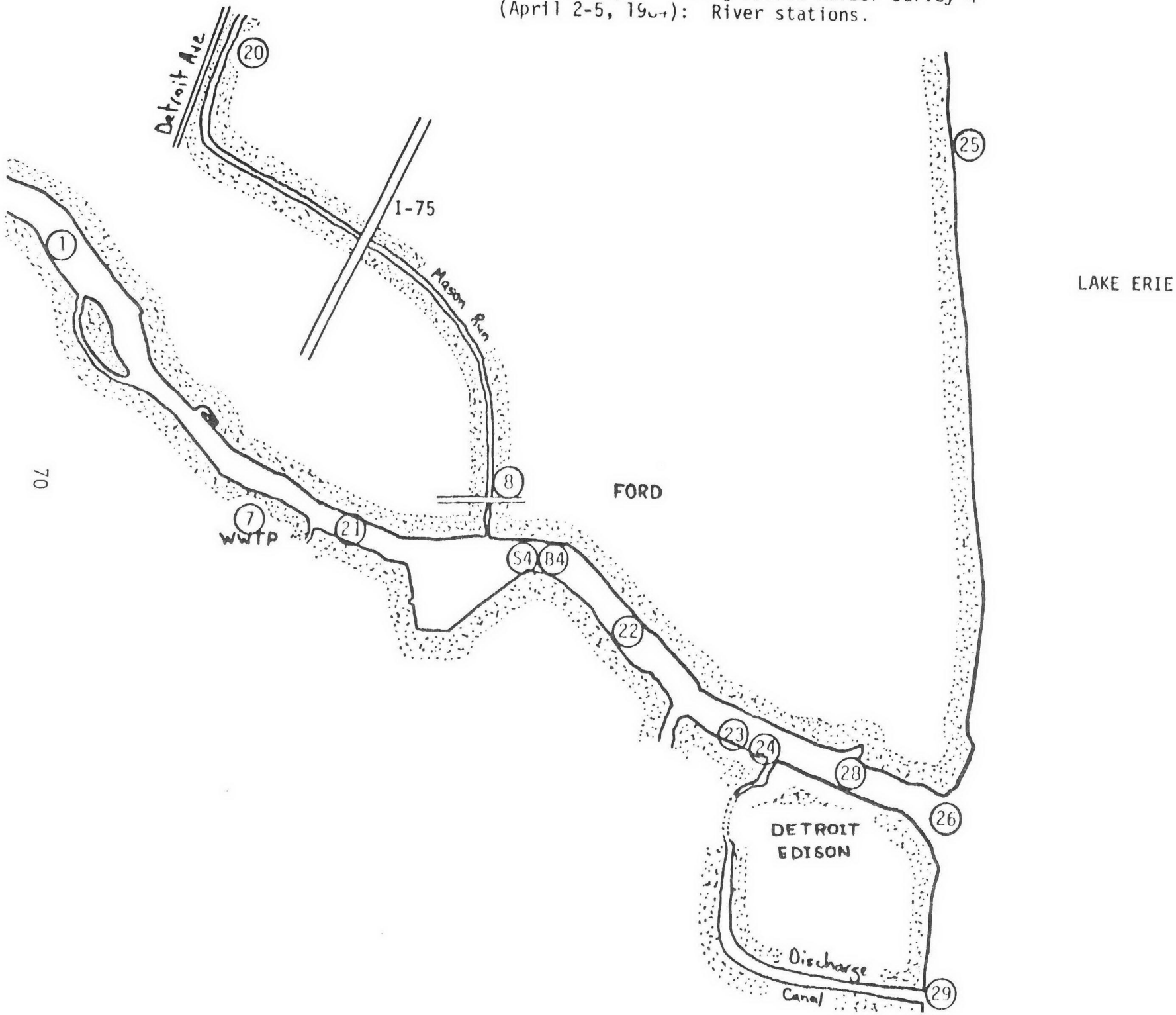


Fig. 3.4b. Stations sampled during Monroe Harbor Survey 4 (April 2-5, 1984): Lake Erie stations.

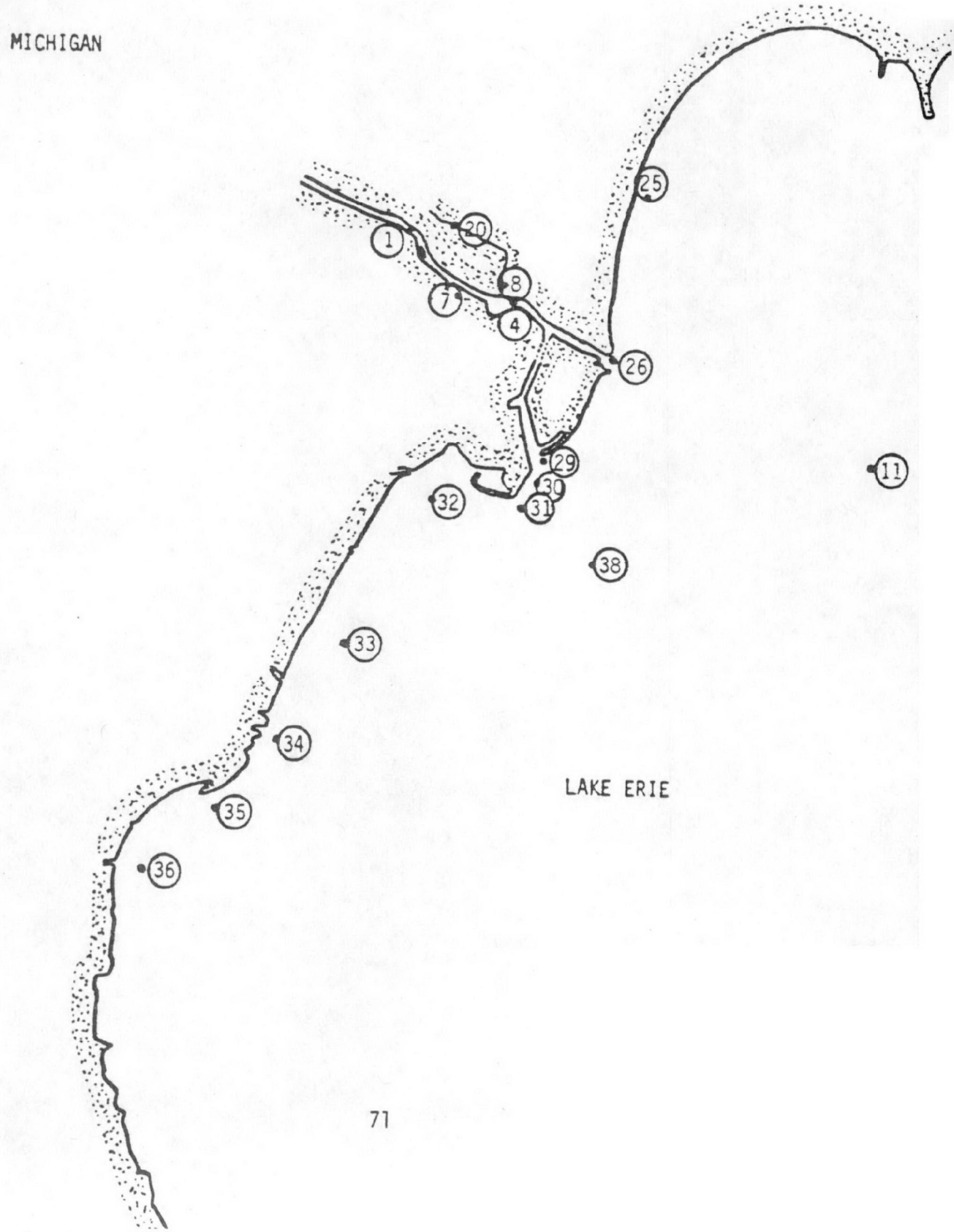


Fig. 3.5a. Stations sampled during Monroe Harbor Survey 5 (May 9, 198[illegible]). River stations.

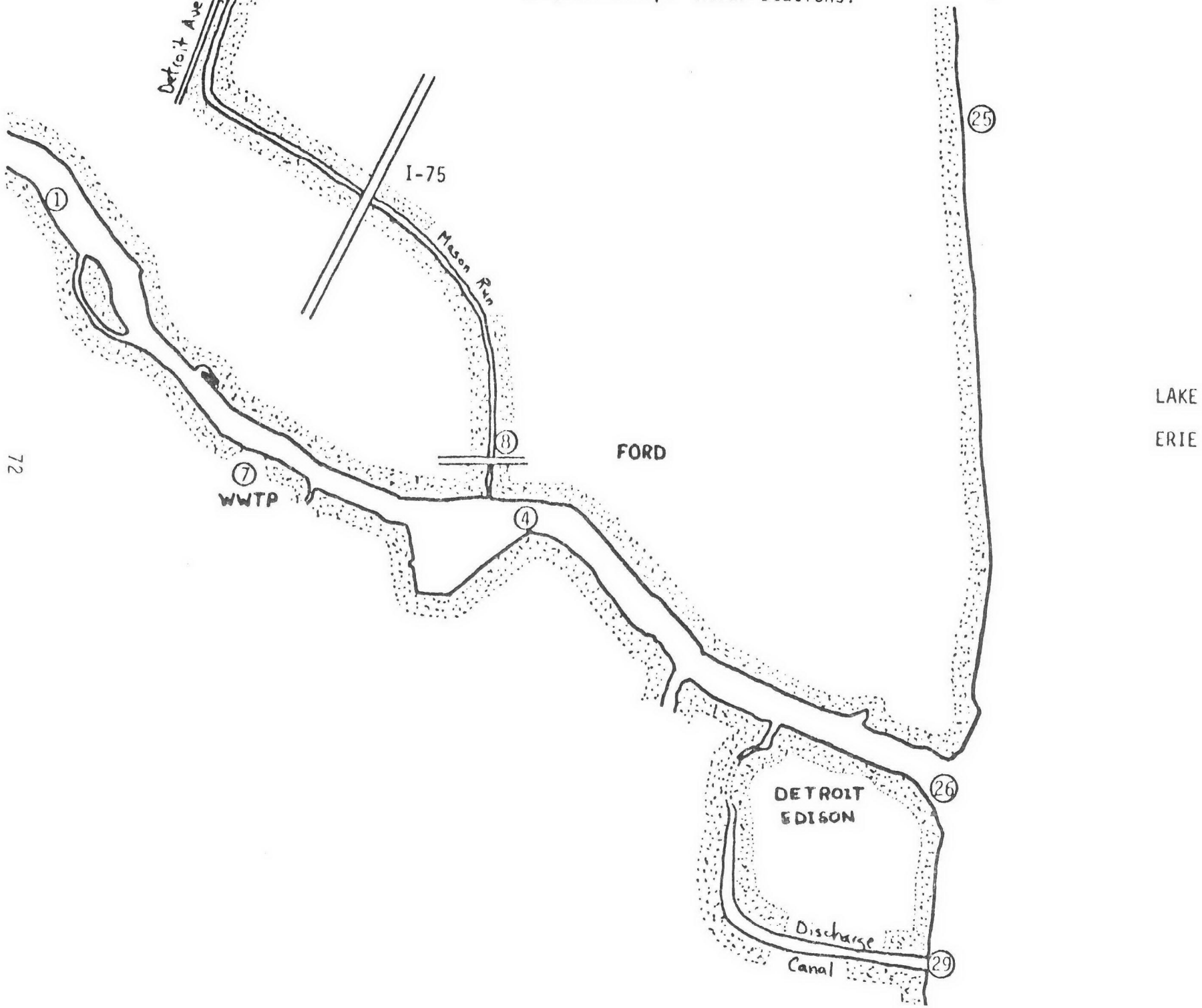


Fig. 3.5b. Stations sampled during Harbor Survey 5 (May 9, 1984): Lake Erie stations.

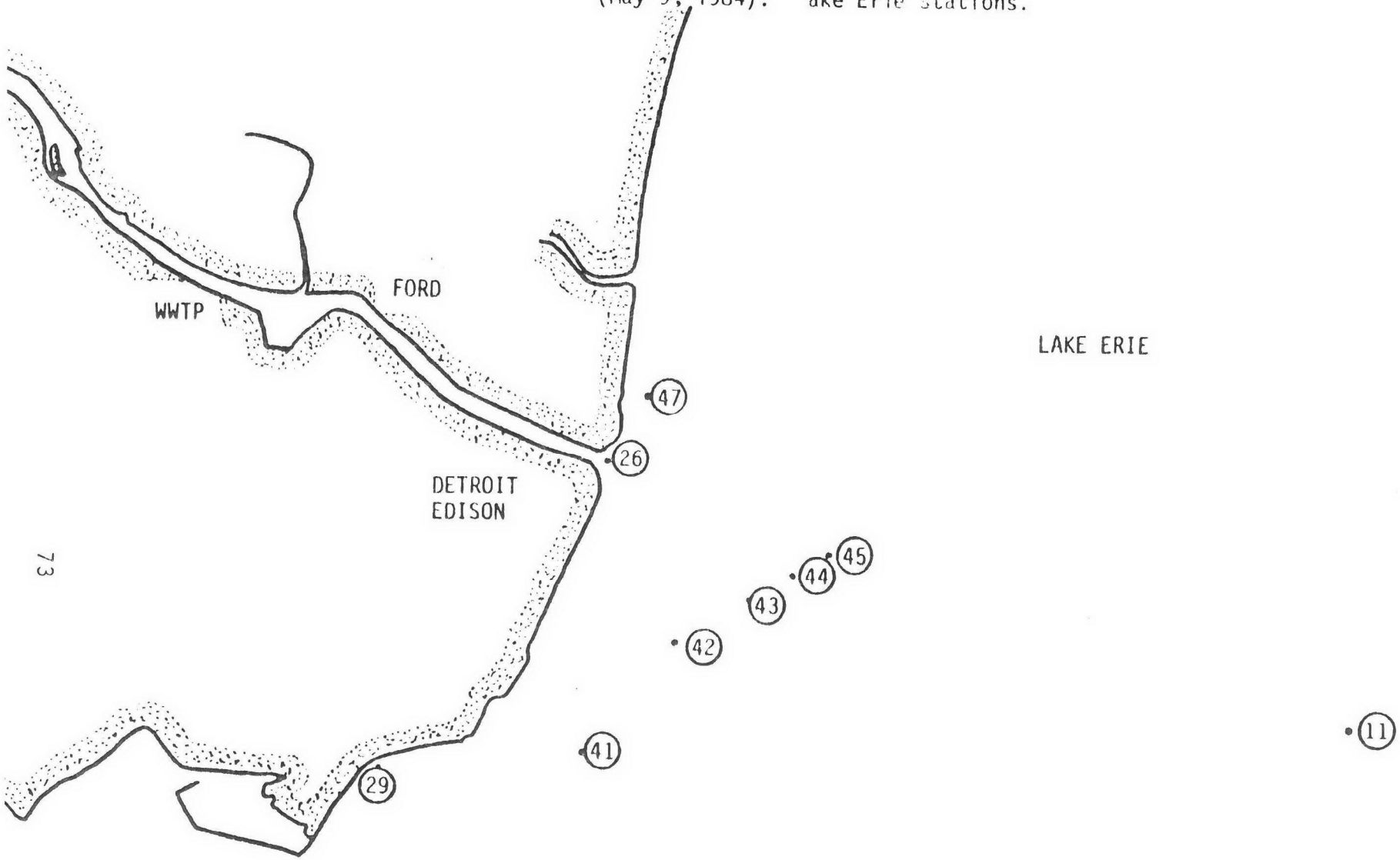
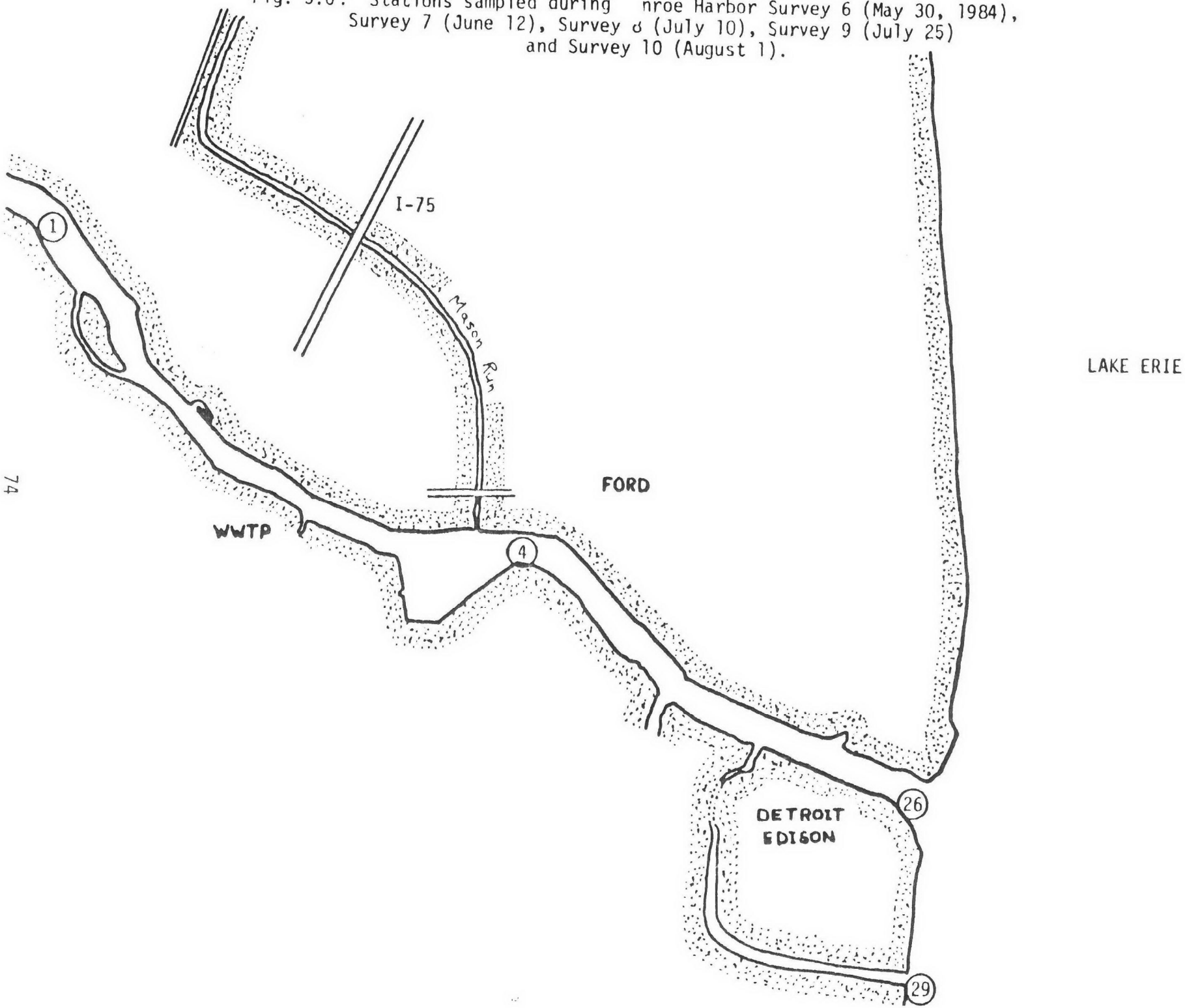
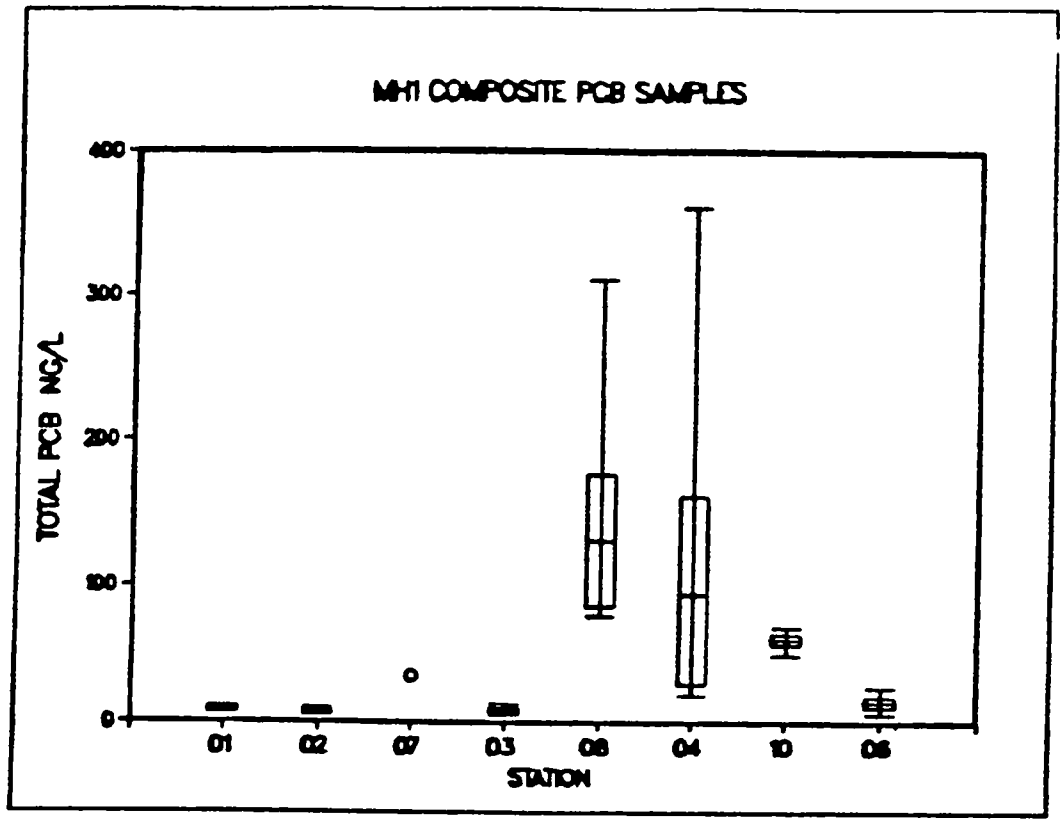
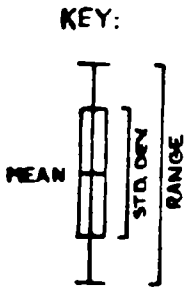


Fig. 3.6. Stations sampled during nroe Harbor Survey 6 (May 30, 1984), Survey 7 (June 12), Survey 8 (July 10), Survey 9 (July 25) and Survey 10 (August 1).







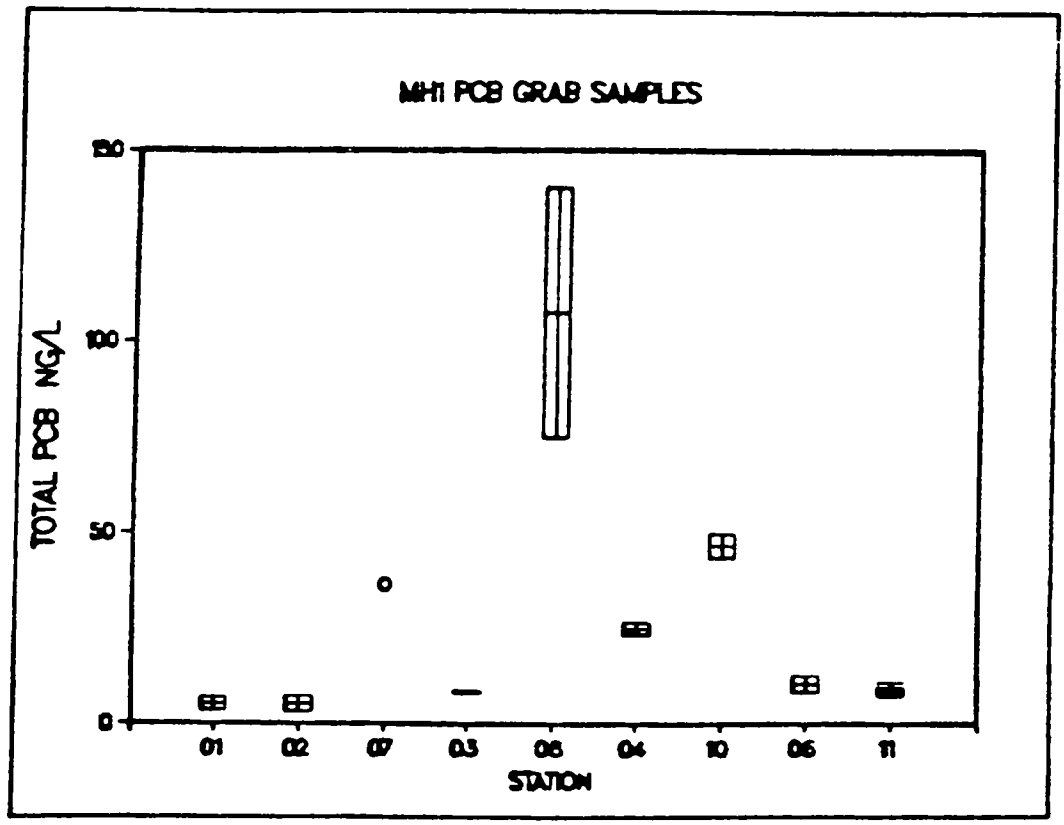


Figure 4.1. Spatial profile of total PCB in composite (a) and grab (b) whole water samples. Monroe Harbor, Survey 1. (See map, Figure 2.1).

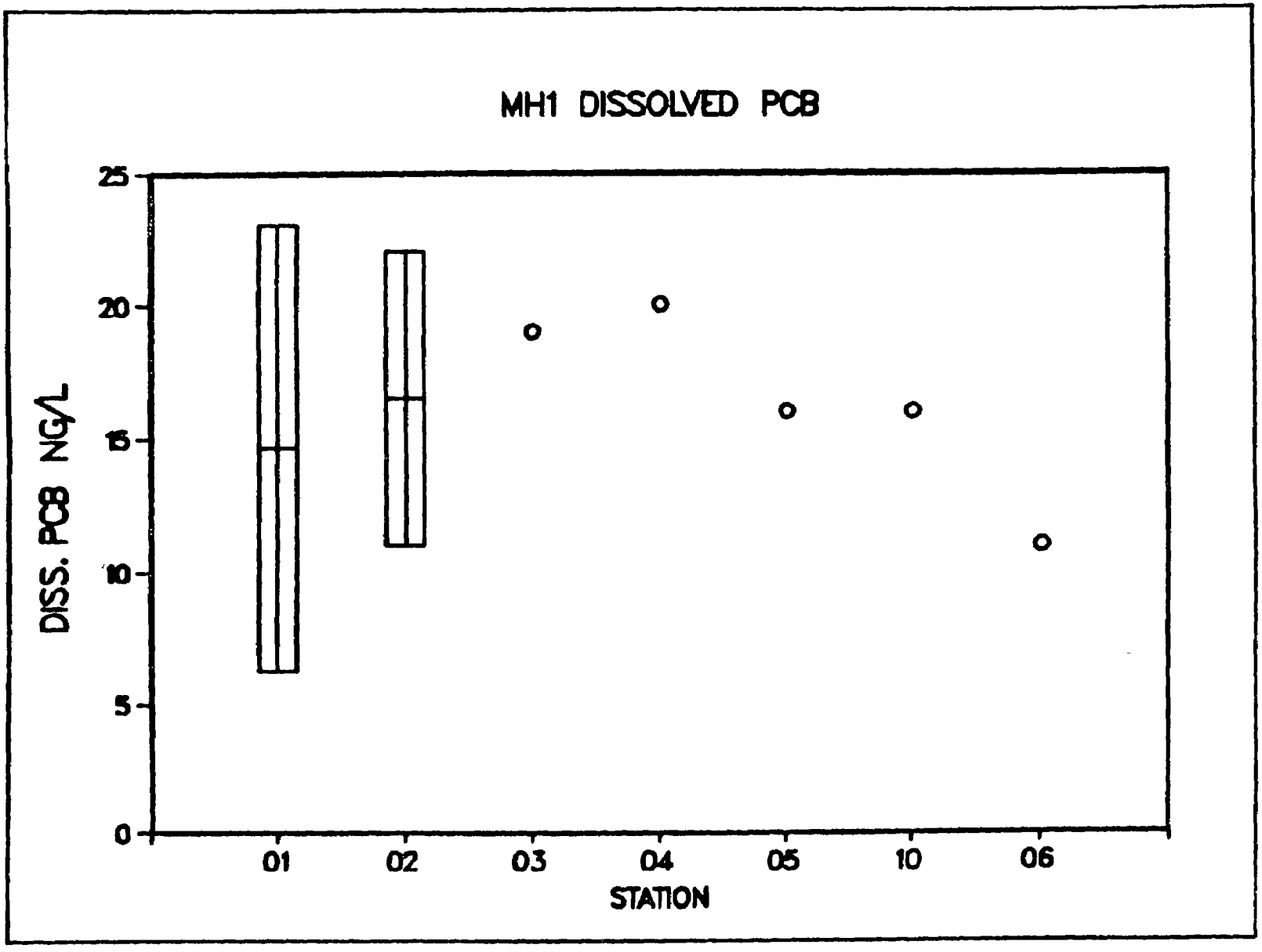


Figure 4.2. Spatial profile of total PCB in composite filtrate water samples. Monroe Harbor, Survey 1. (See map, Figure 2.1).

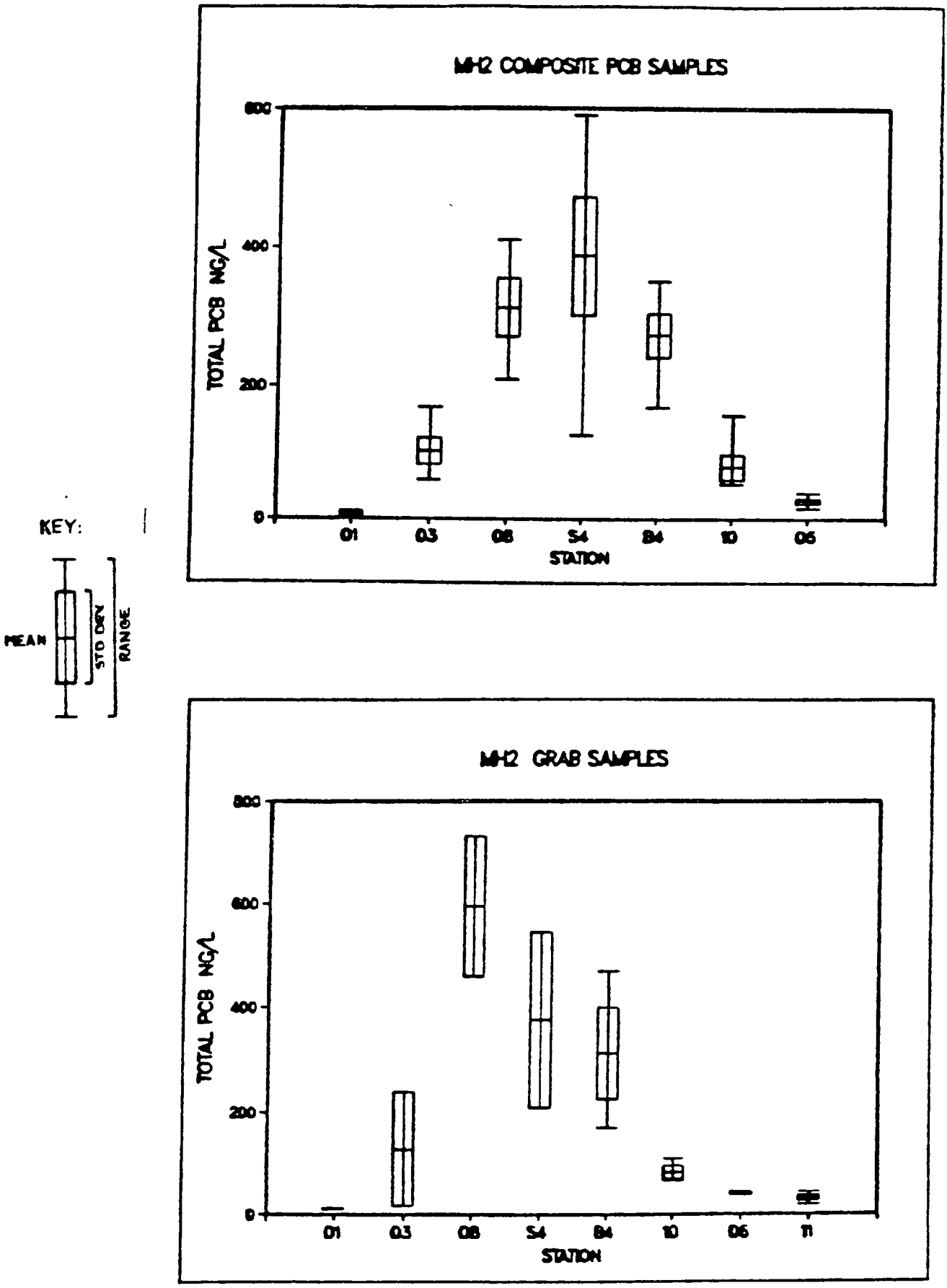


Figure 4.3. Spatial profile of total PCB in composite (a) and grab (b) whole water samples. Monroe Harbor, Survey 2. (See map, Figure 2.2).

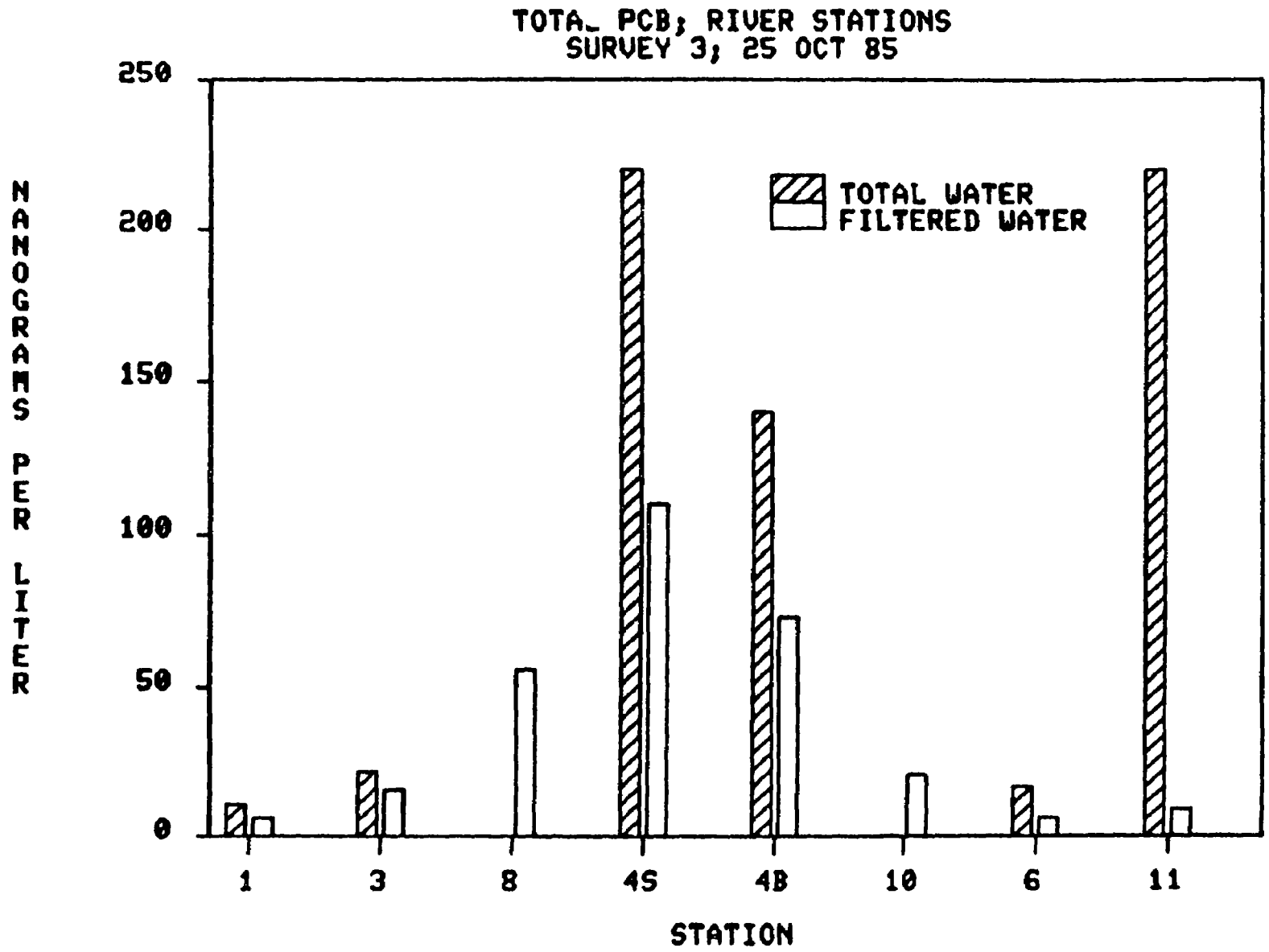
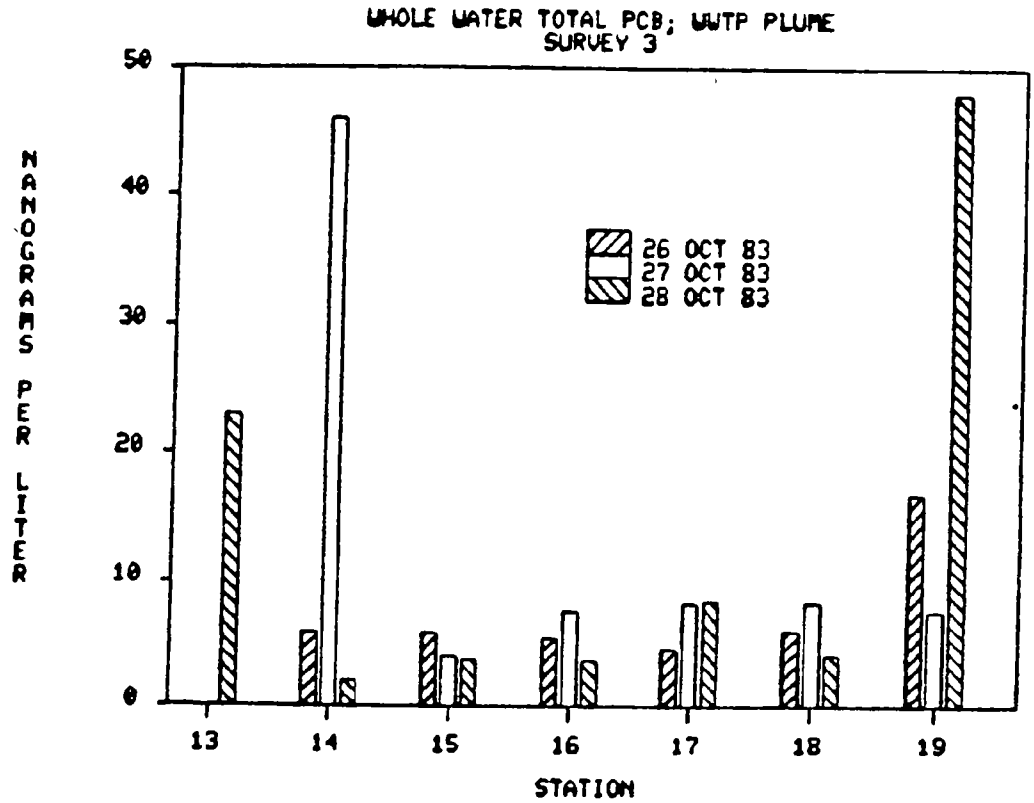


Figure 4.4. Spatial profile of total PCB in composite whole water and filtrate water. Monroe Harbor, Survey 3. (See map, Figure 2.3).



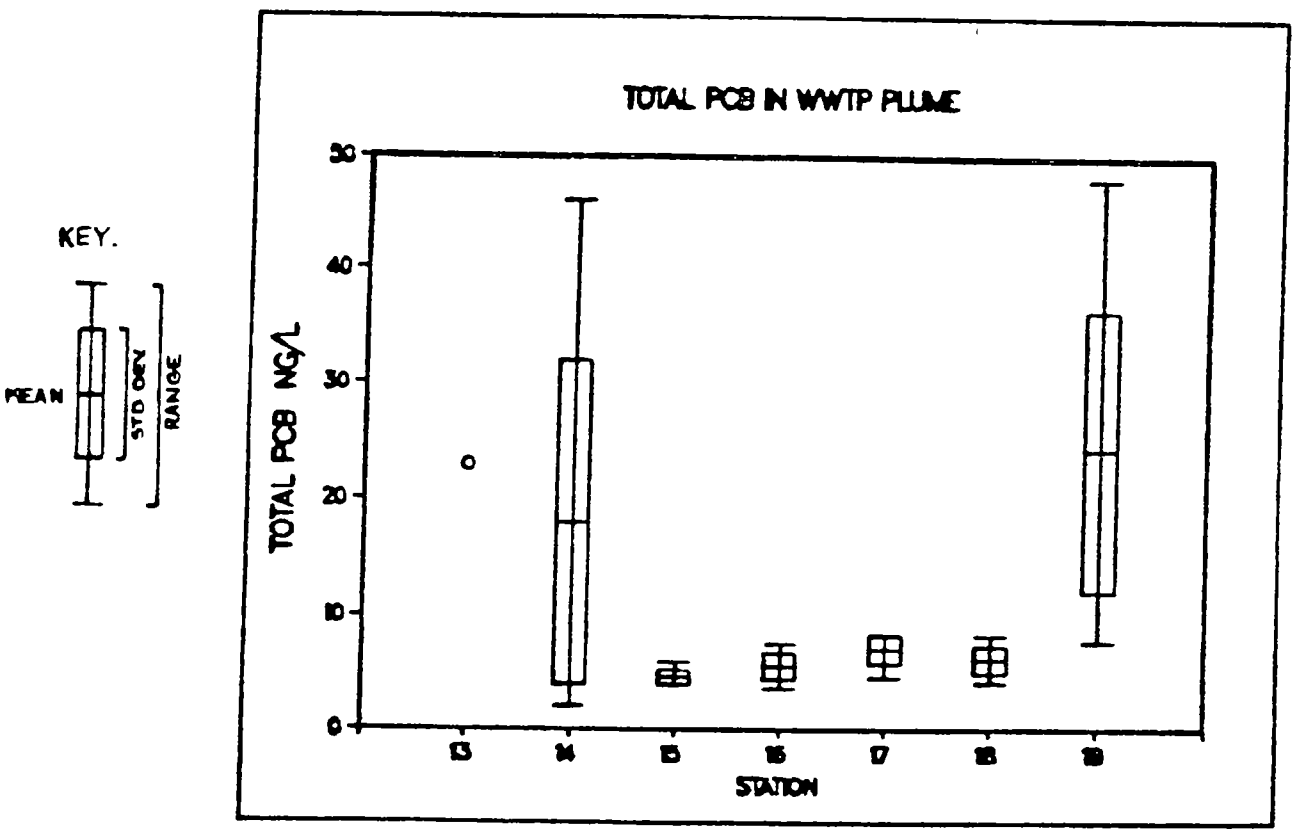


Figure 4.5. Spatial profile of total PCB in grab whole water samples. Monroe Harbor WWTP plume, Survey 3; daily concentrations (a) and station averages (b). (See map, Figure 2.3).

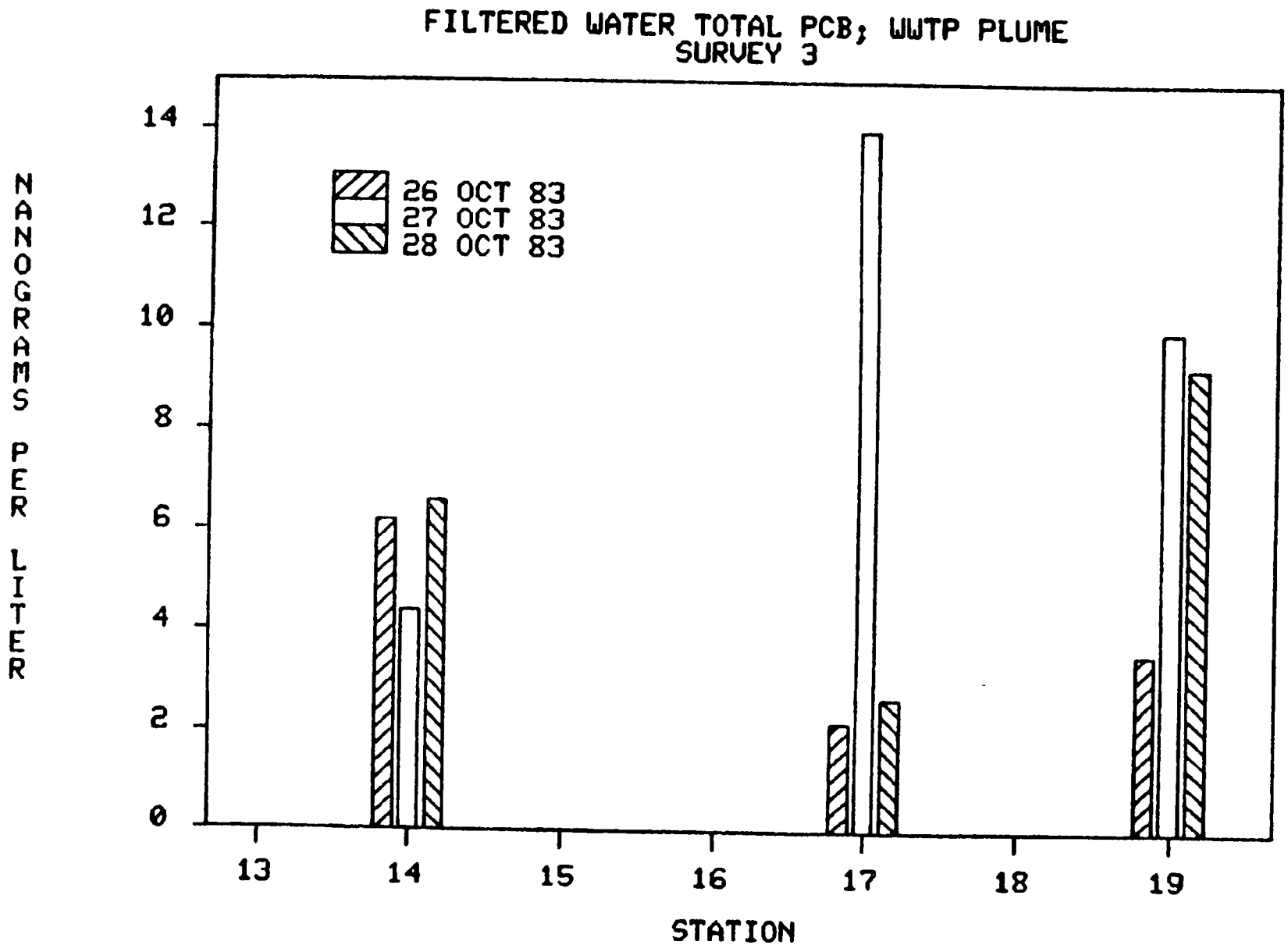


Figure 4.6. Spatial profile of total PCB in grab filtrate water samples. Monroe Harbor, Survey 3. (See map, Figure 2.3).

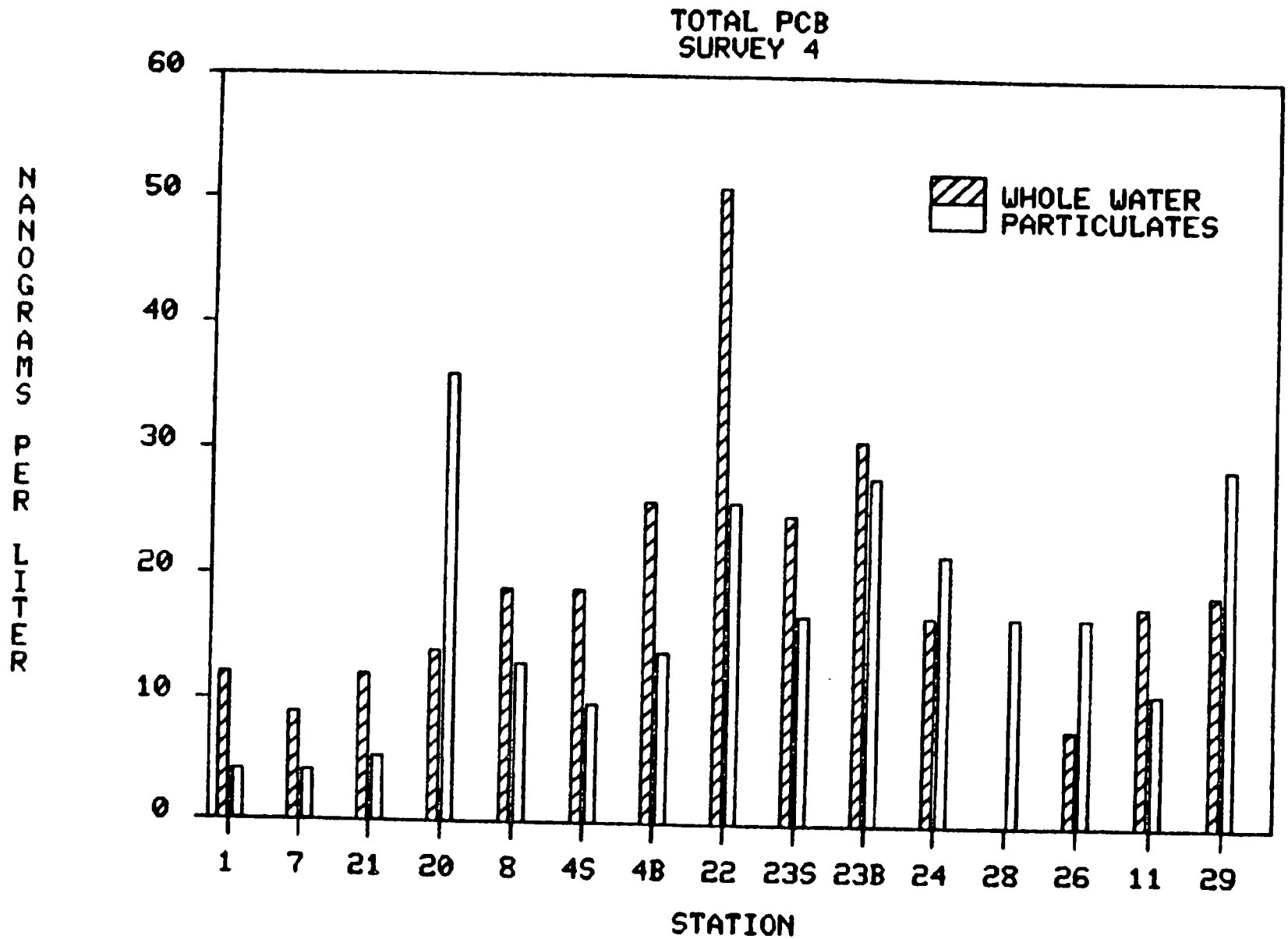


Figure 4.7. Spatial profile of total PCB in whole water particulate grab samples. Monroe Harbor, Survey 4. (See map, Figure 2.4).

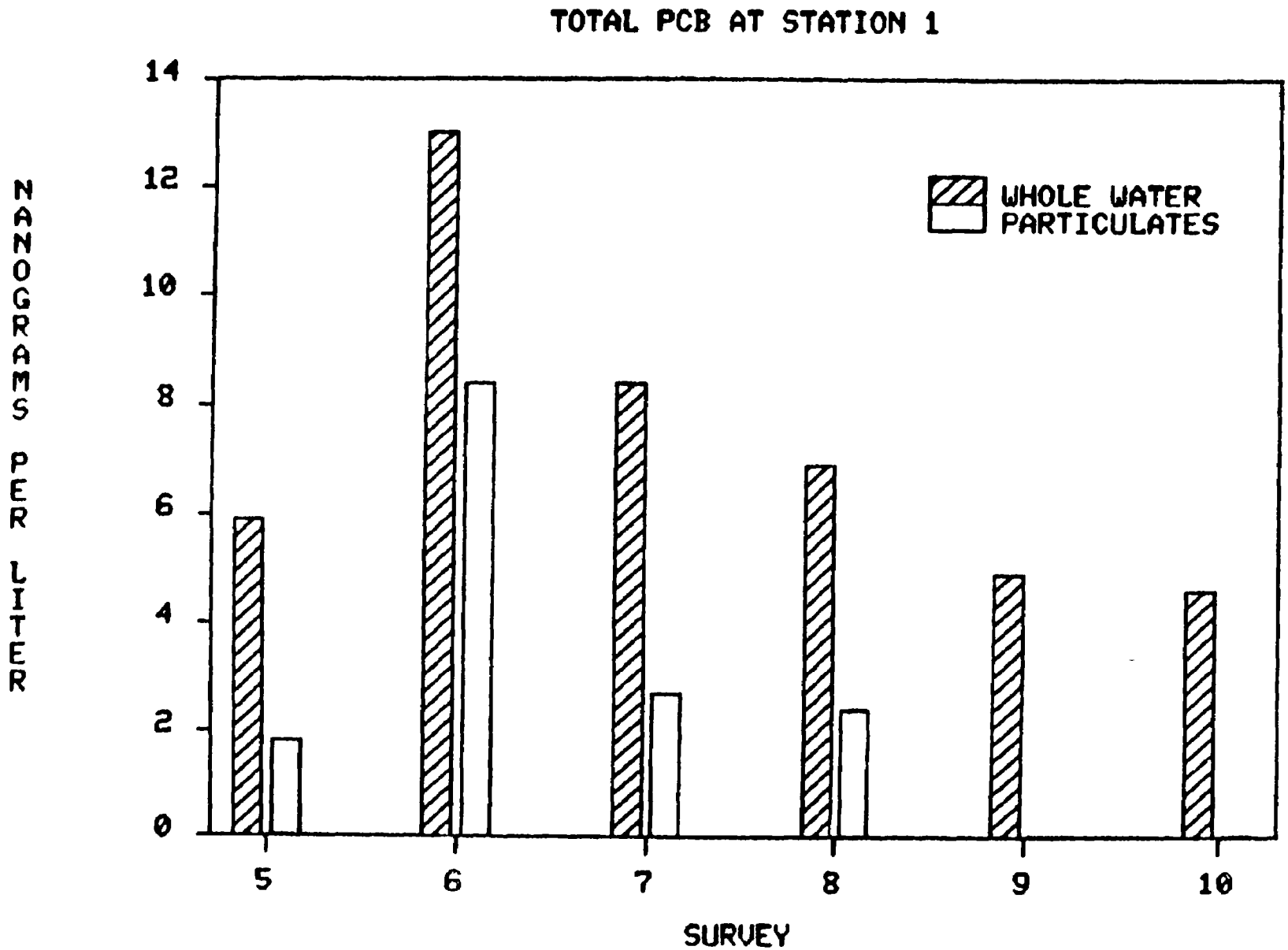


Figure 4.8. Temporal profile of total PCB in grab whole water and particulate samples at Station 1. Monroe Harbor, Surveys 5-10. (See map, Figure 2.6).

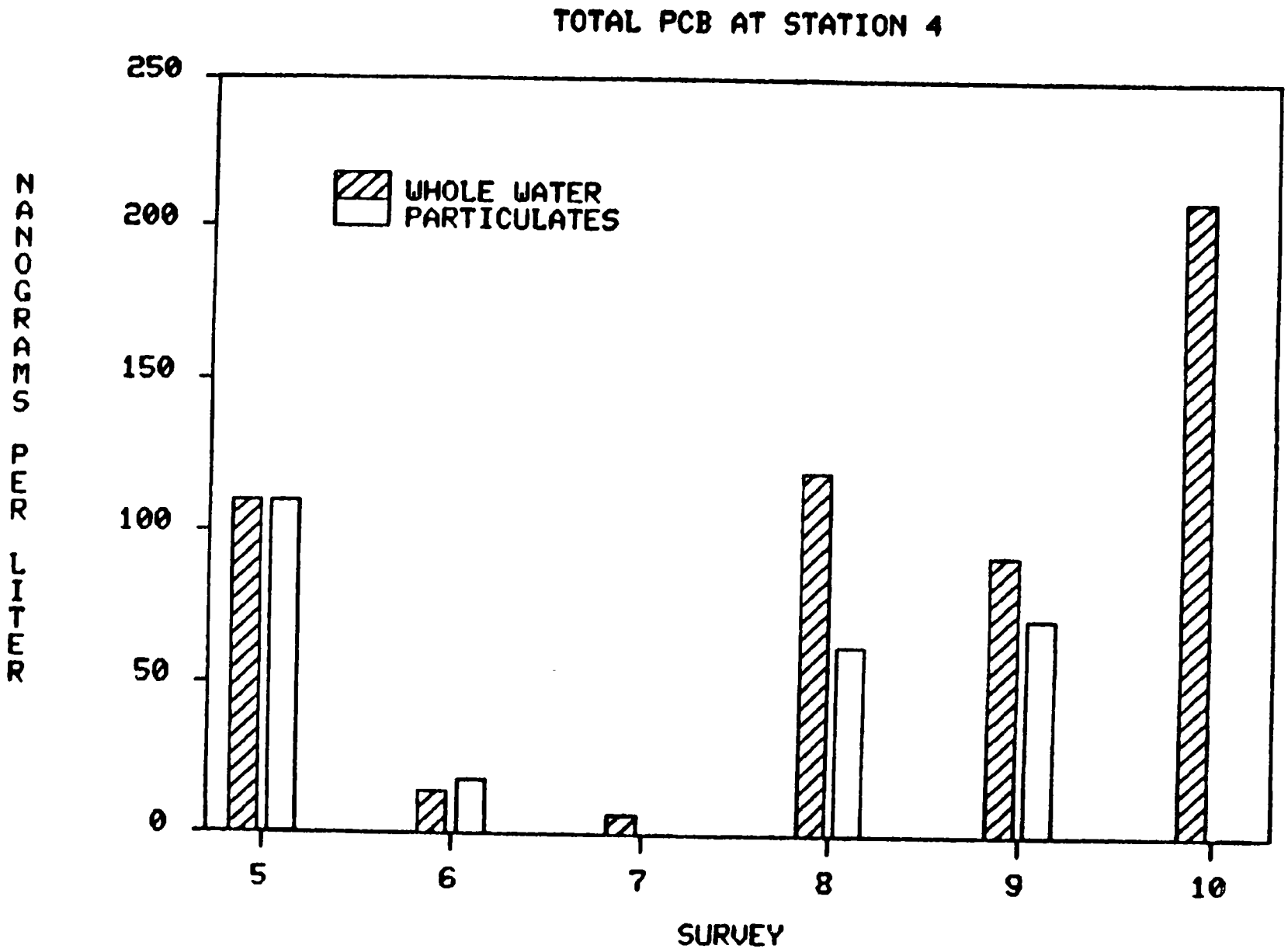


Figure 4.9. Temporal profile of total PCB in grab whole water and particulate samples at Station 4. Monroe Harbor, Surveys 5-10. (See map, Figure 2.6).

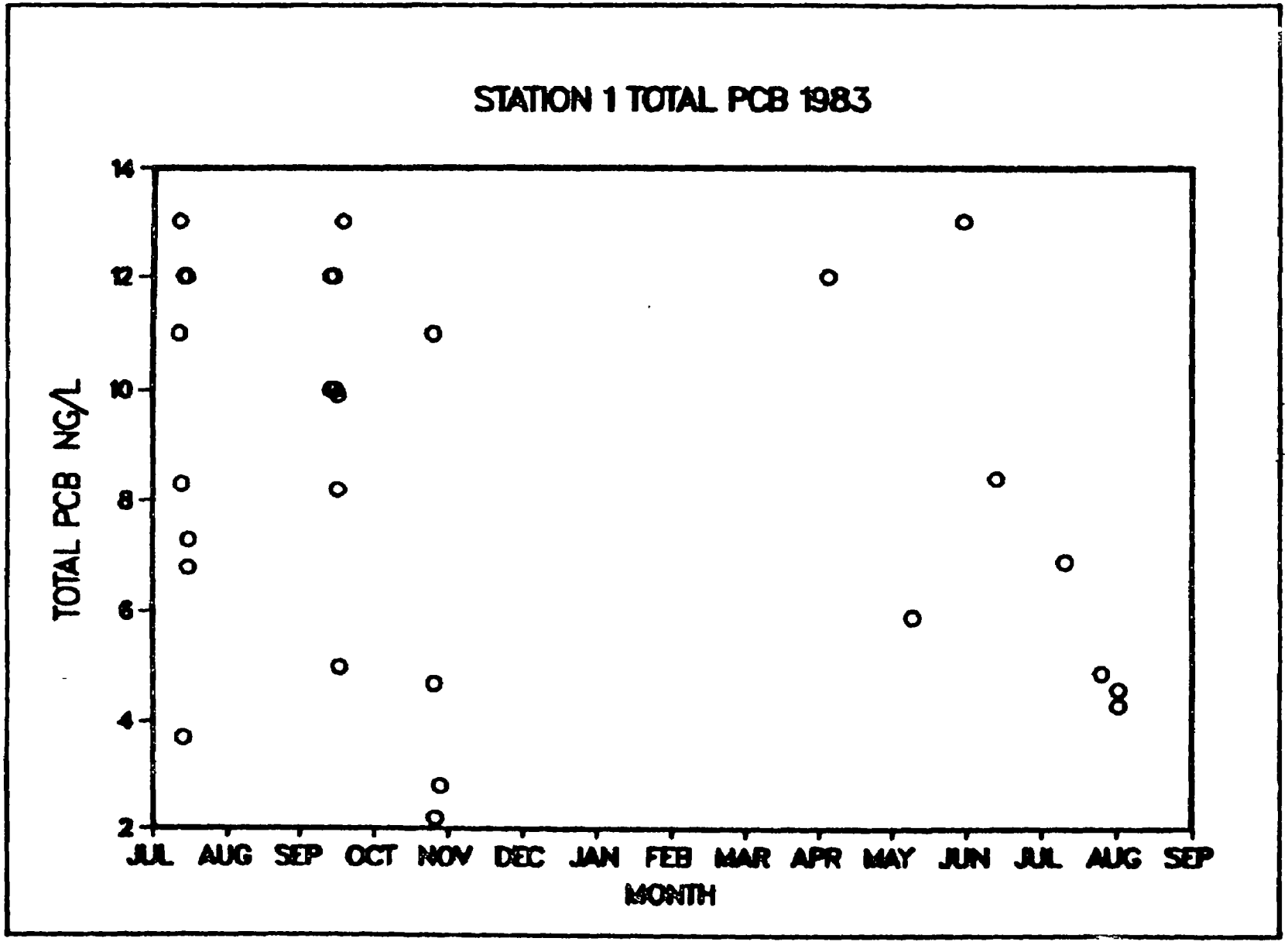


Figure 4.10. Temporal profile of total PCB in all grab and composite whole water samples at Station 1. Monroe Harbor, Surveys 1-10.

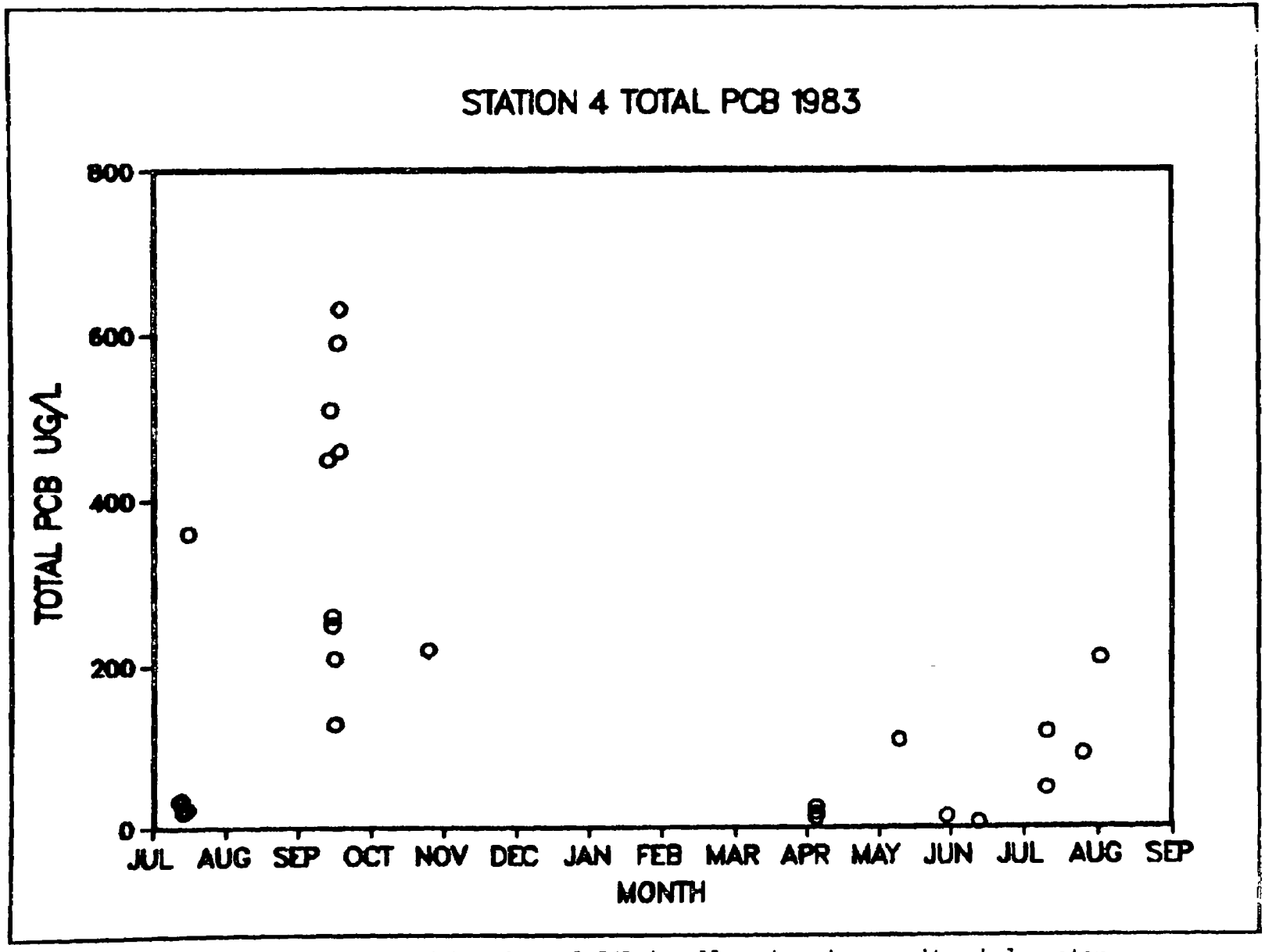


Figure 4.11. Temporal profile of total PCB in all grab and composite whole water samples at Station 4. Monroe Harbor, Surveys 1-10.

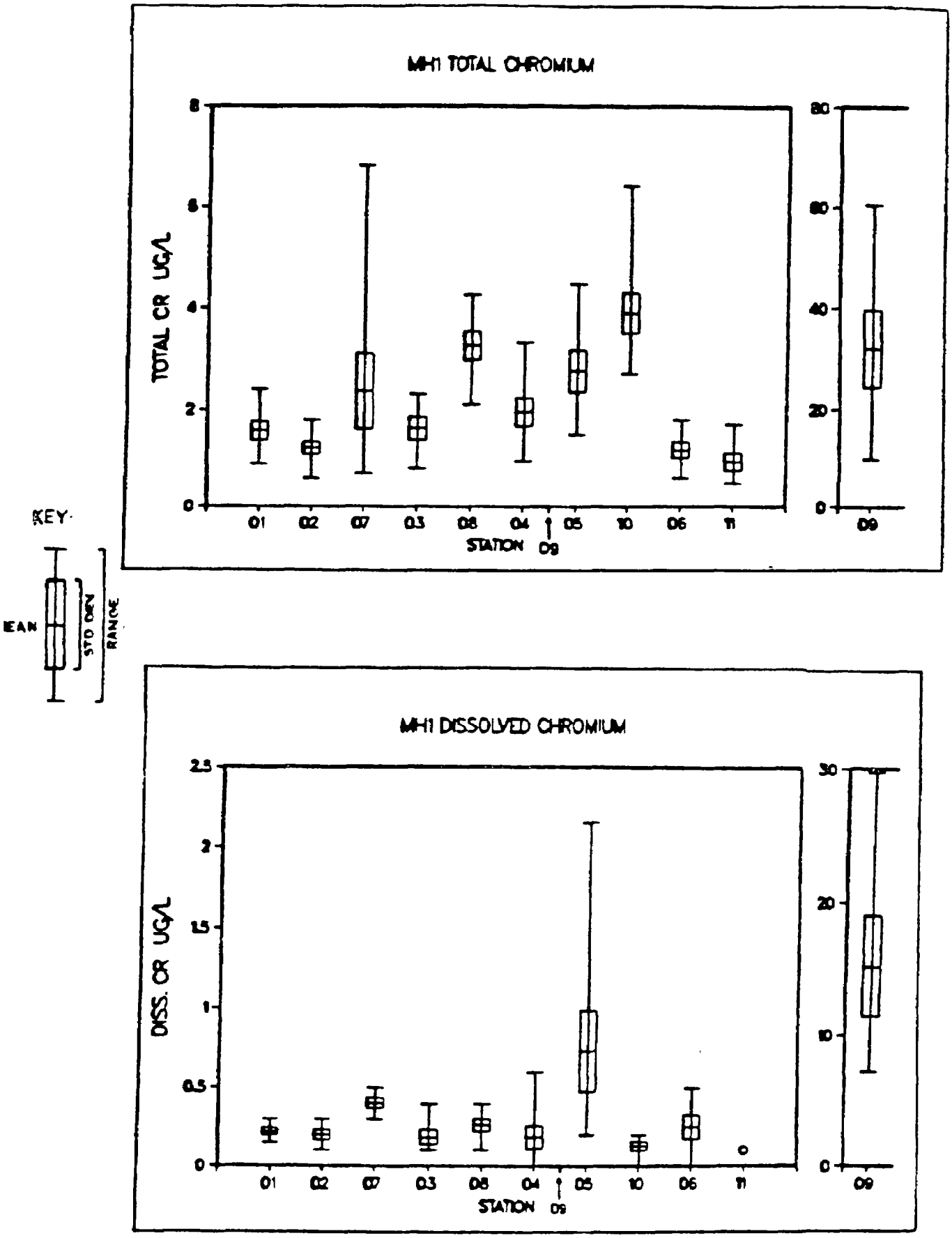
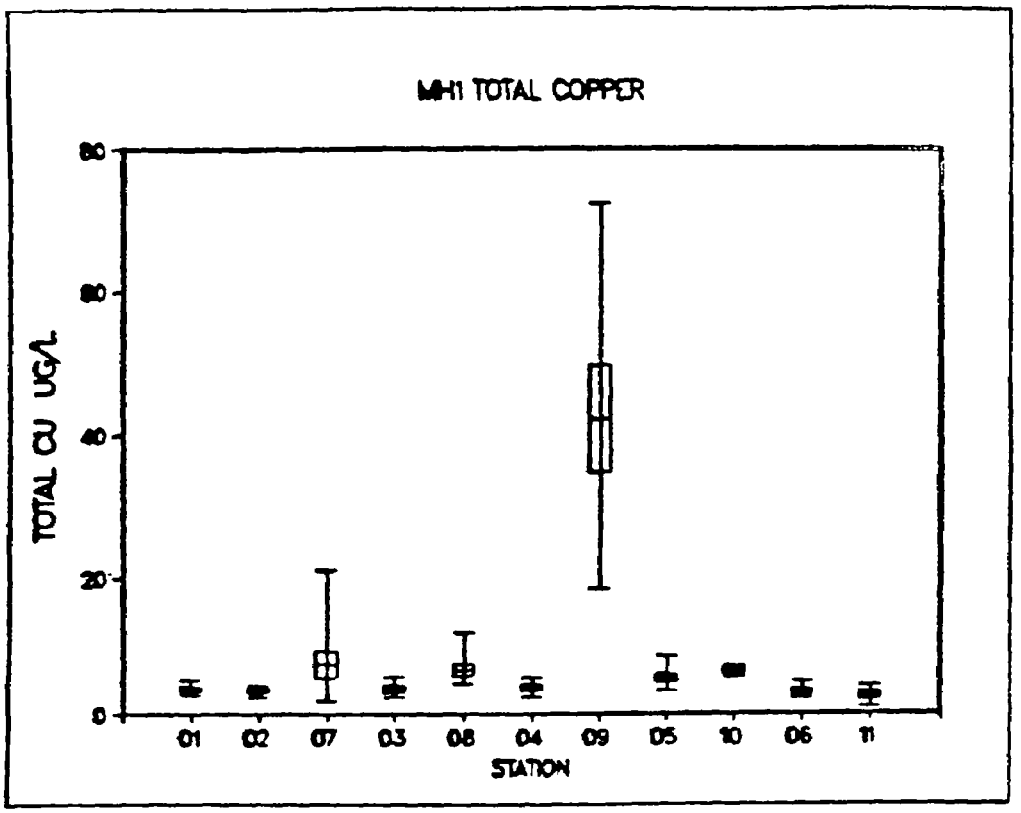
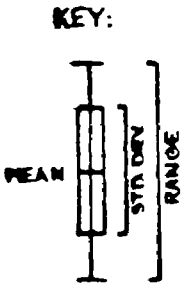


Figure 4.12. Spatial profile of total and dissolved chromium in grab and composite water samples. Monroe Harbor, Survey 1. (See map, Figure 2.1).





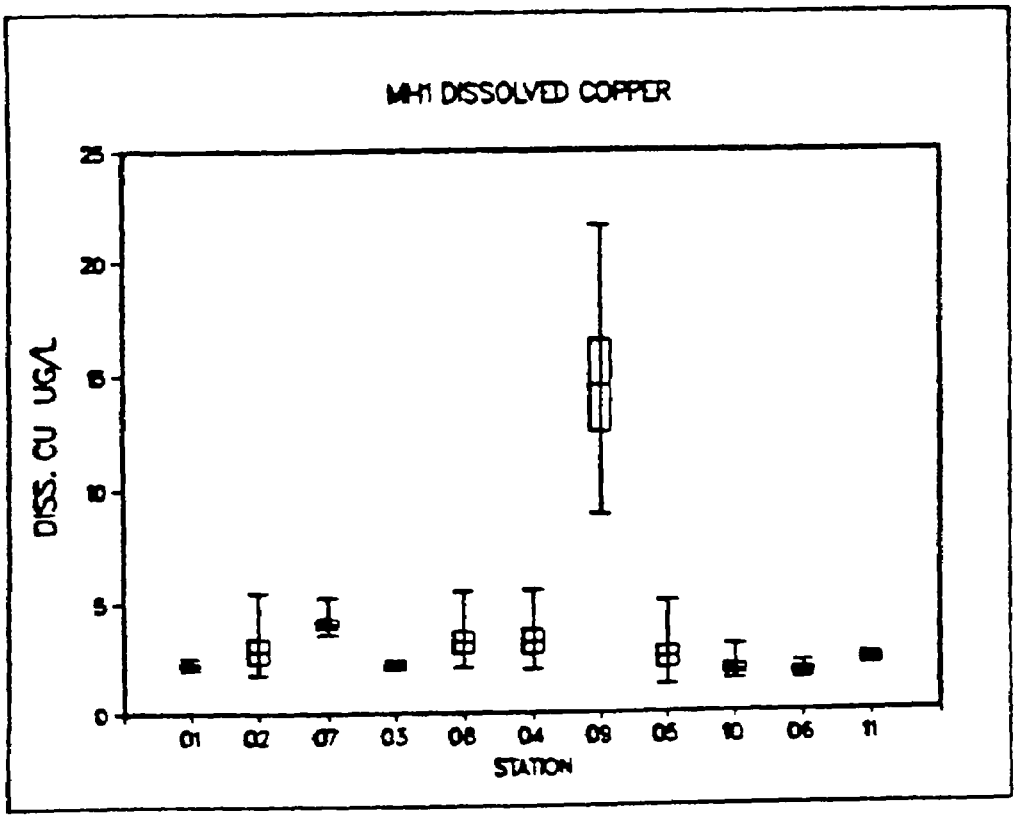


Figure 4.13. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 1. (See map, Figure 2.1).

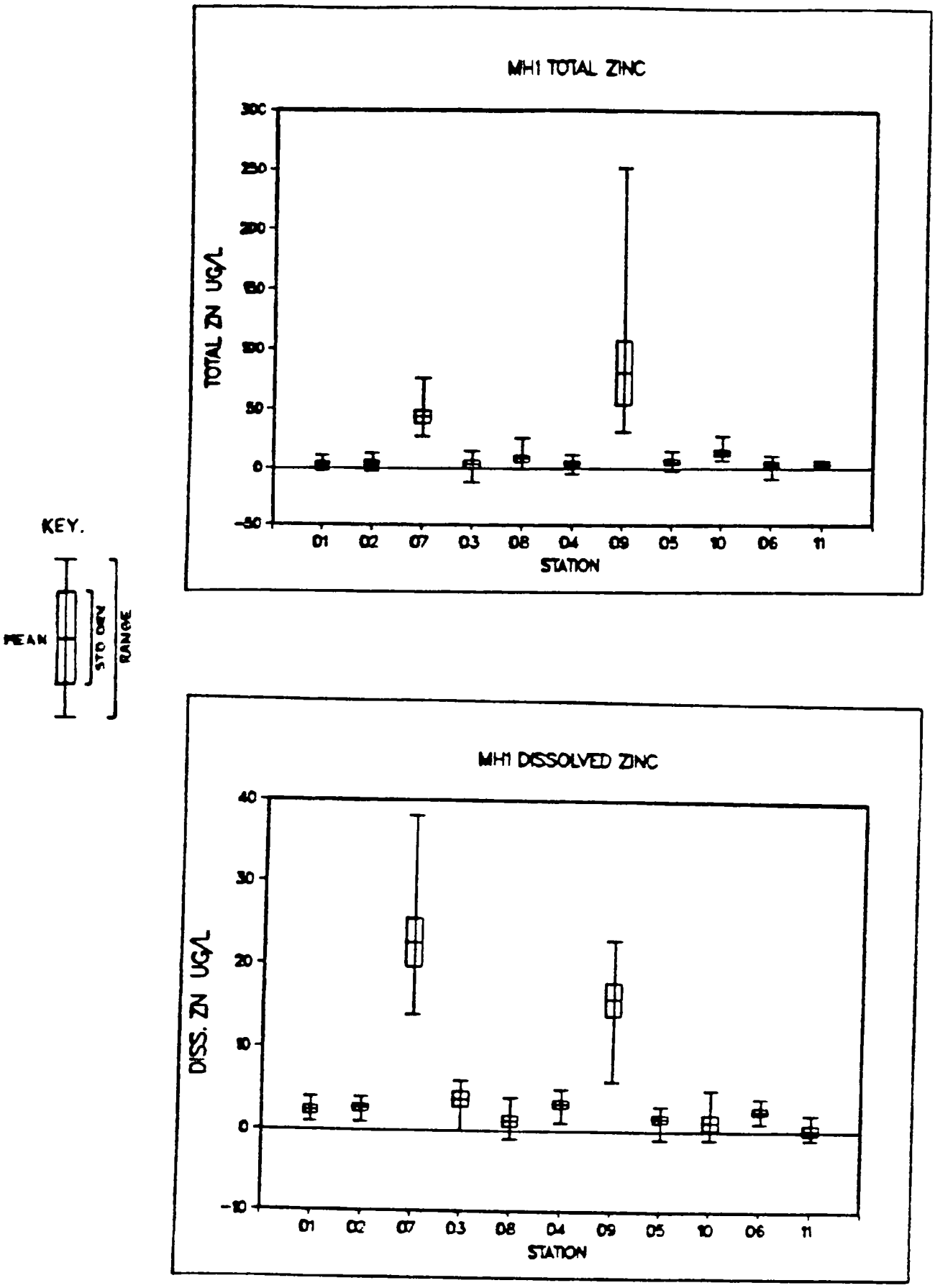


Figure 4.14. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 1. (See map, Figure 2.1).

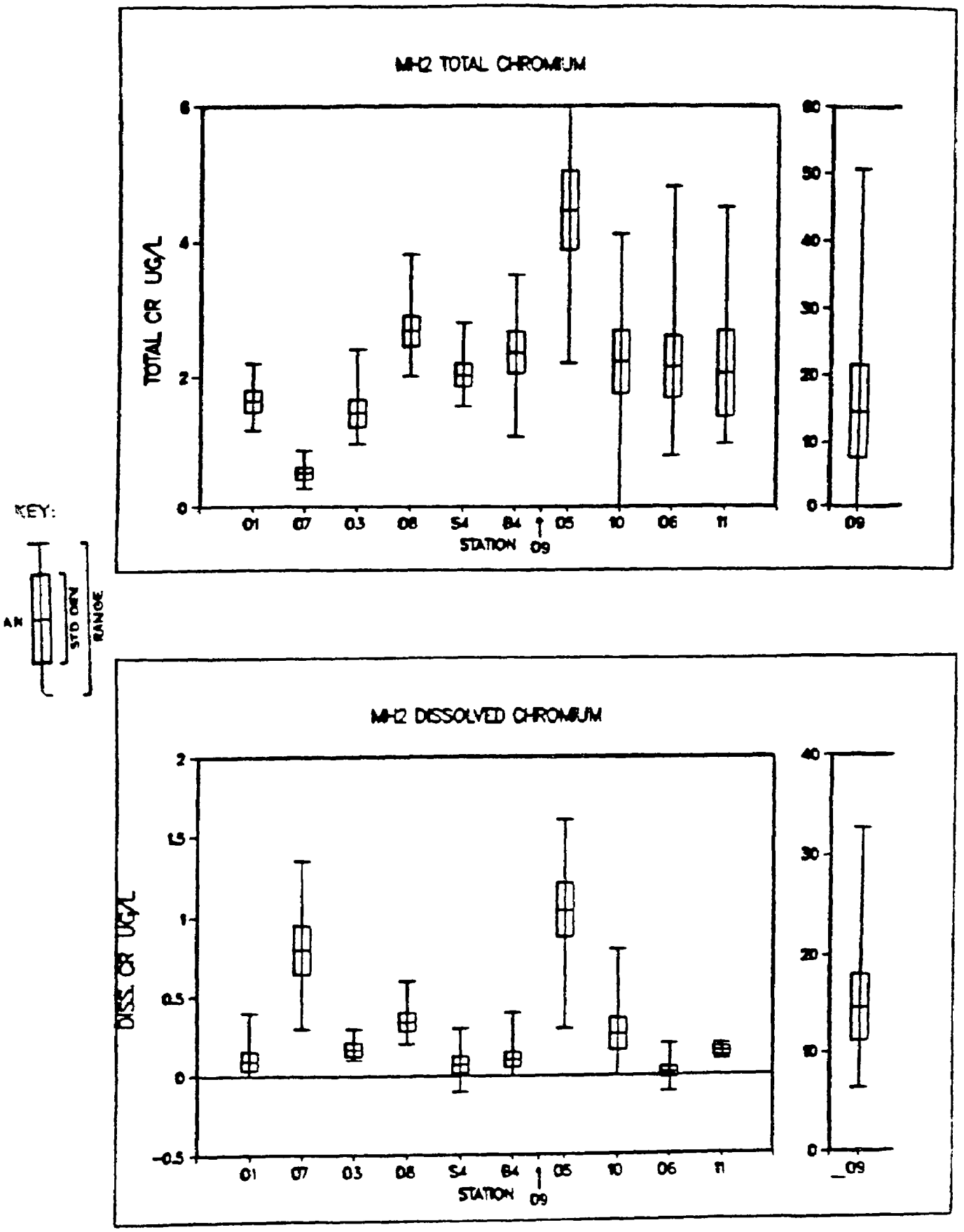


Figure 4.15. Spatial profile of total and dissolved chromium in grab and composite water samples. Monroe Harbor, Survey 2. (See map, Figure 2.2).

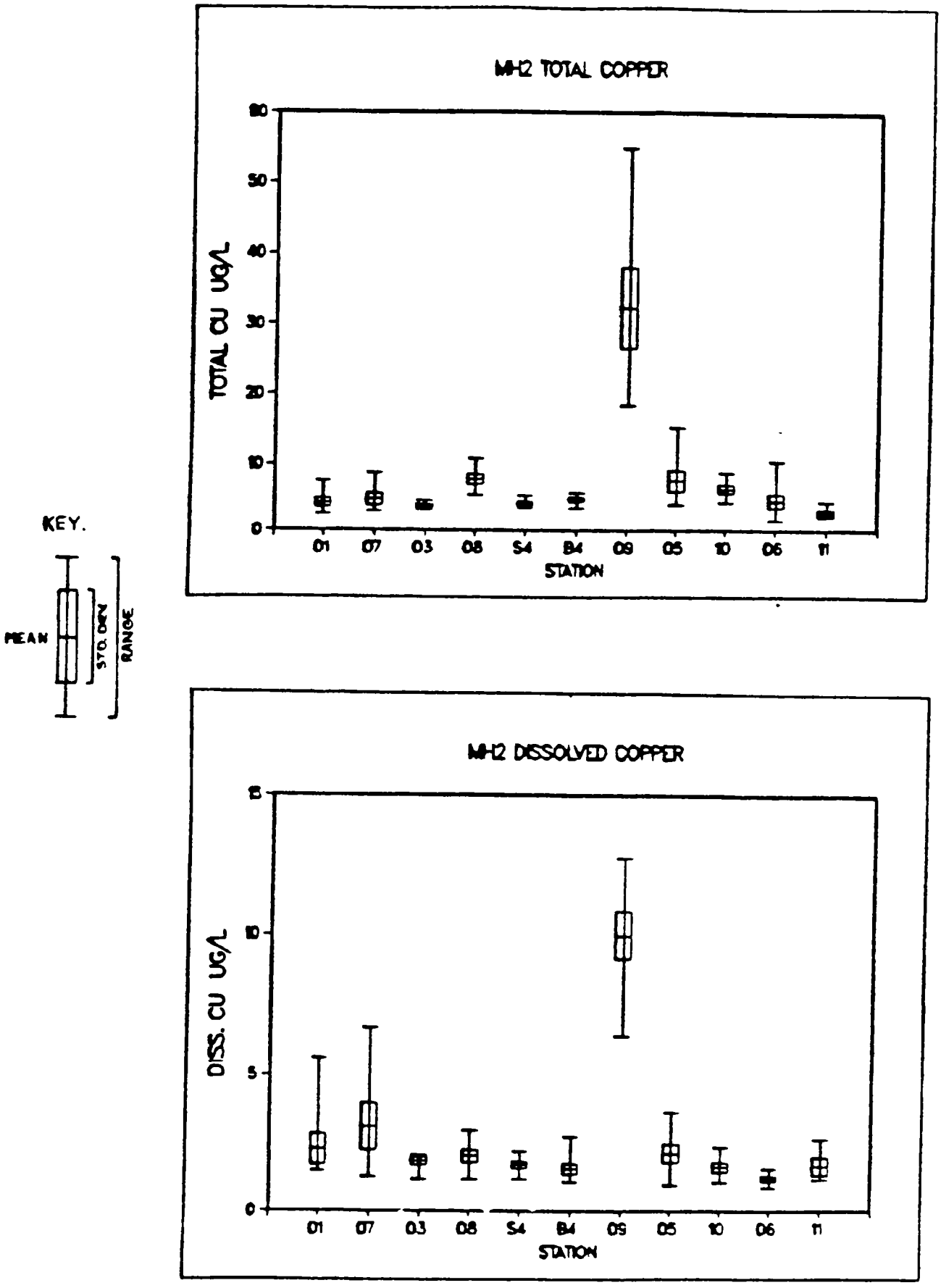


Figure 4.16. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 2. (See map, Figure 2.2).

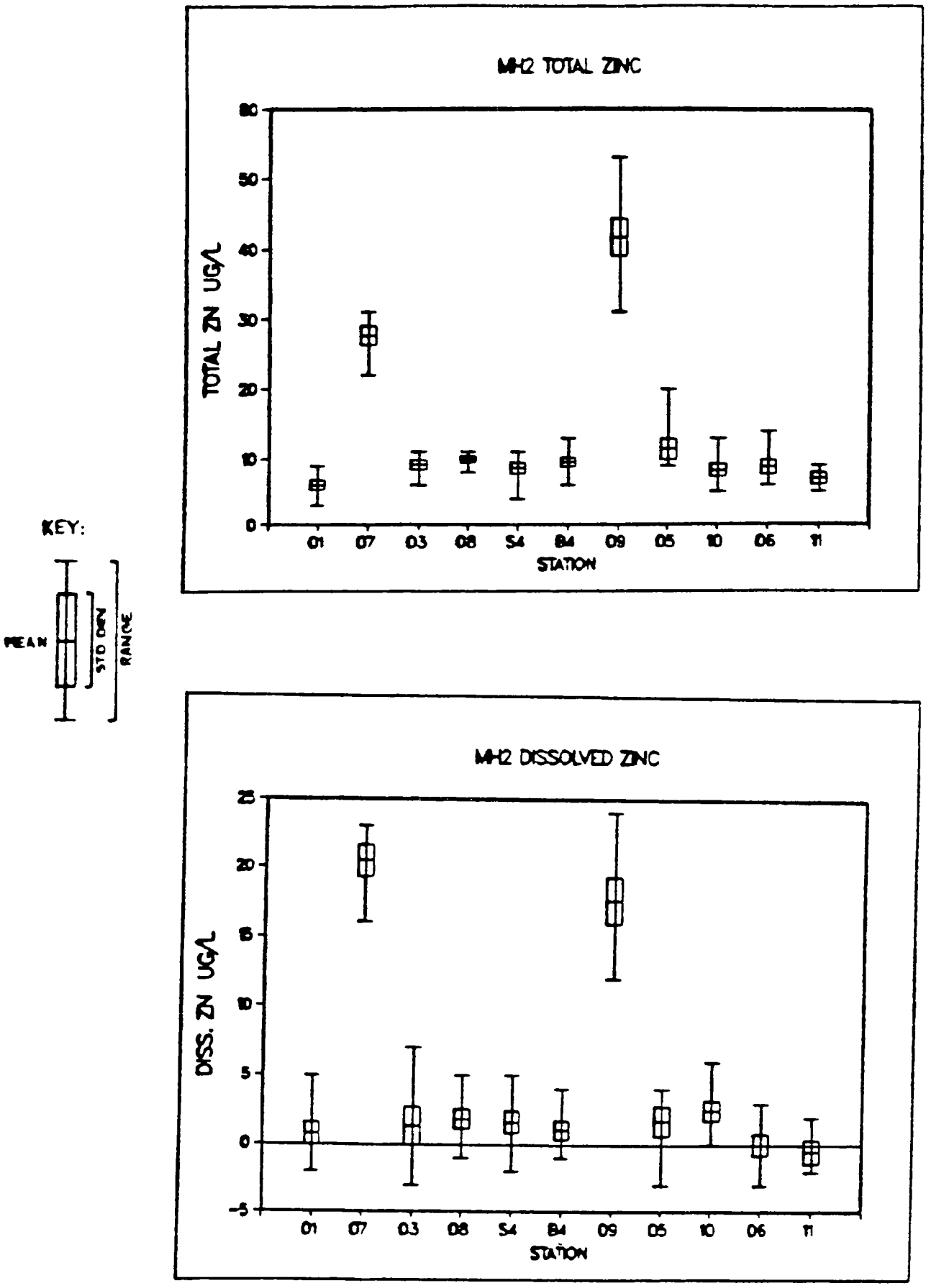
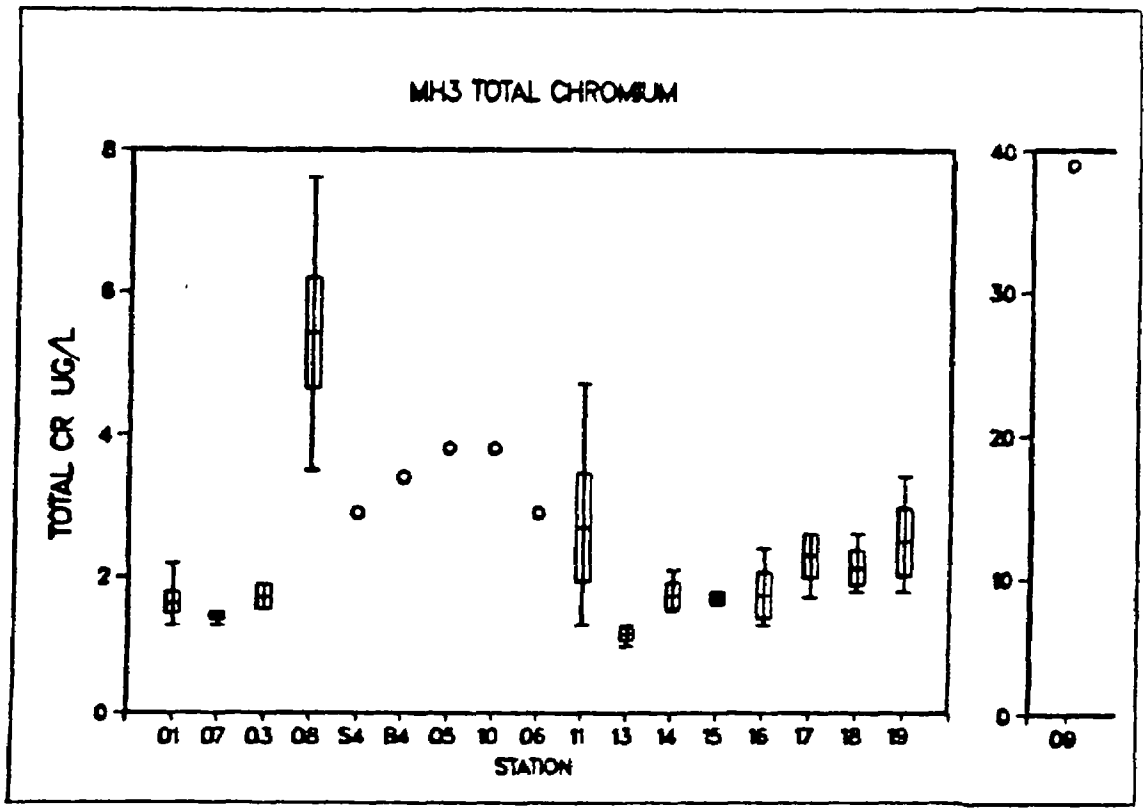
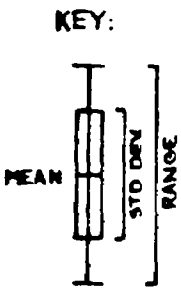


Figure 4.17. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 2. (See map, Figure 2.2).





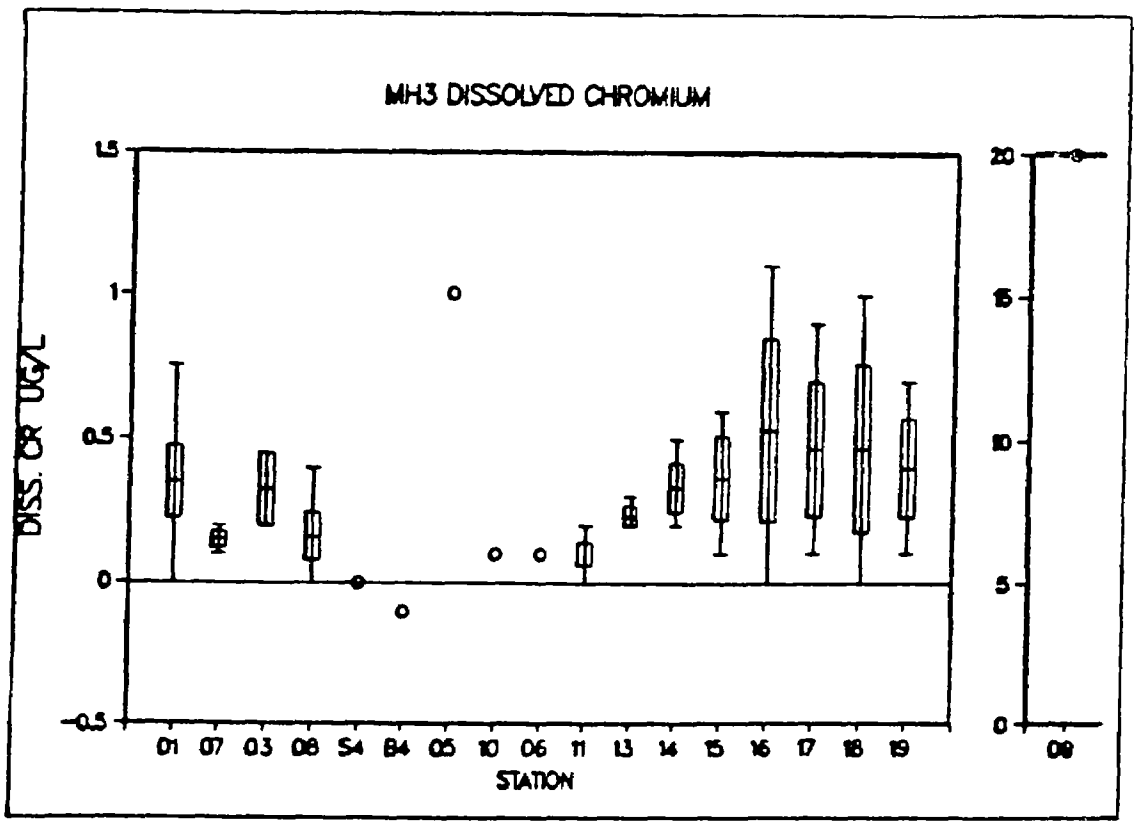
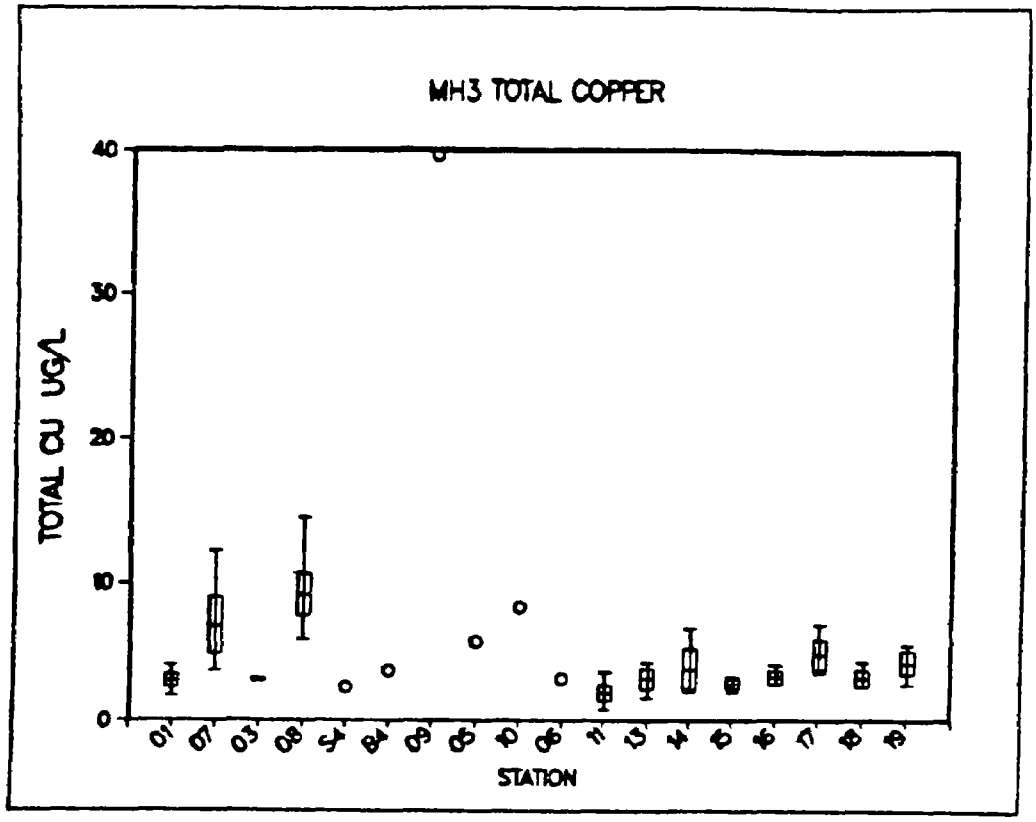


Figure 4.18. Spatial profile of total and dissolved chromium in grab and composite water samples. Monroe Harbor, Survey 3. (See map, Figure 2.3).



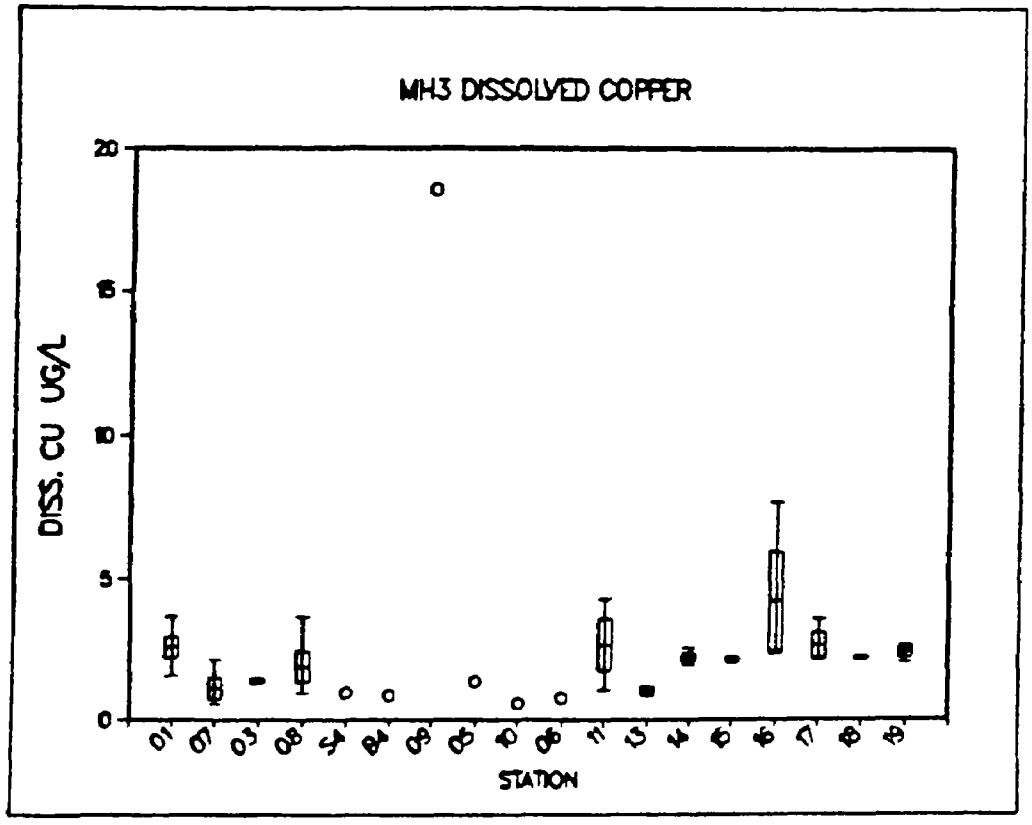
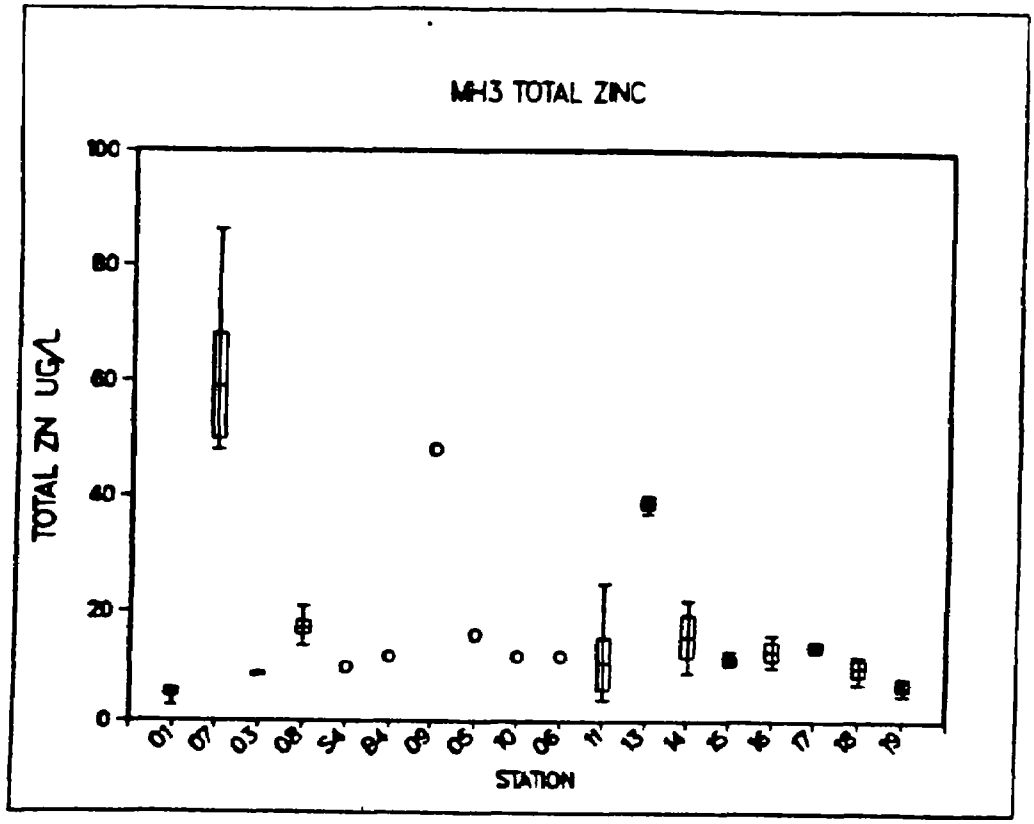


Figure 4.19. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 3. (See map, Figure 2.3).



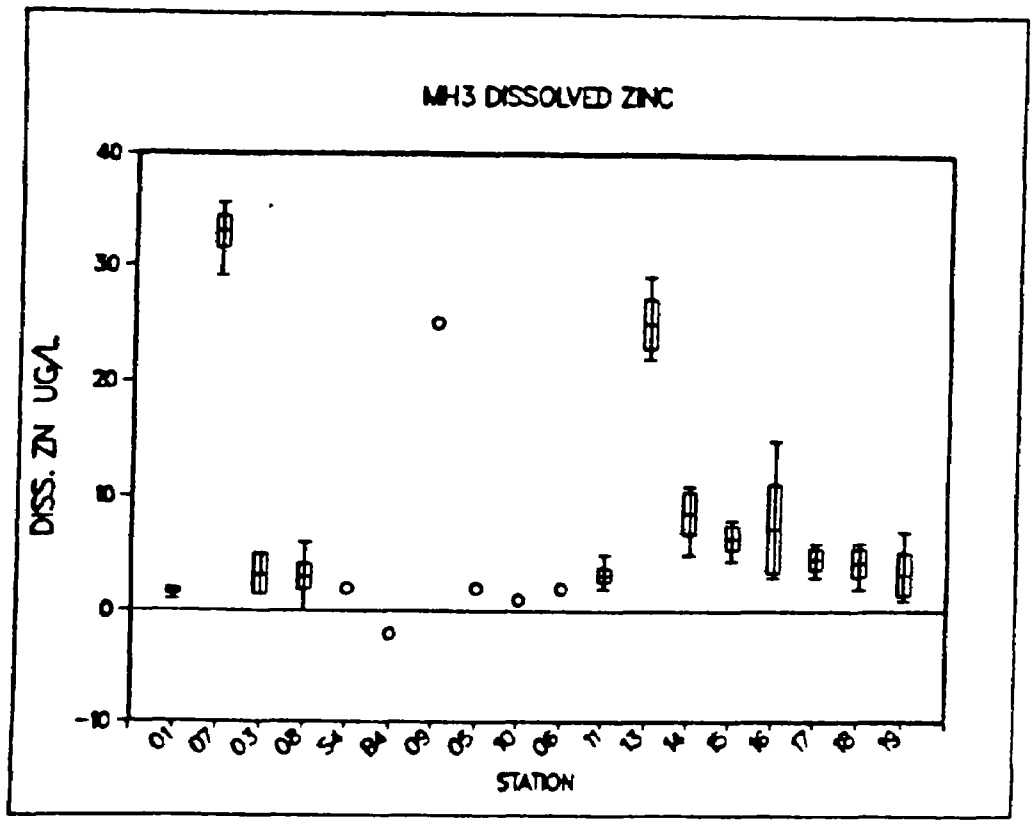
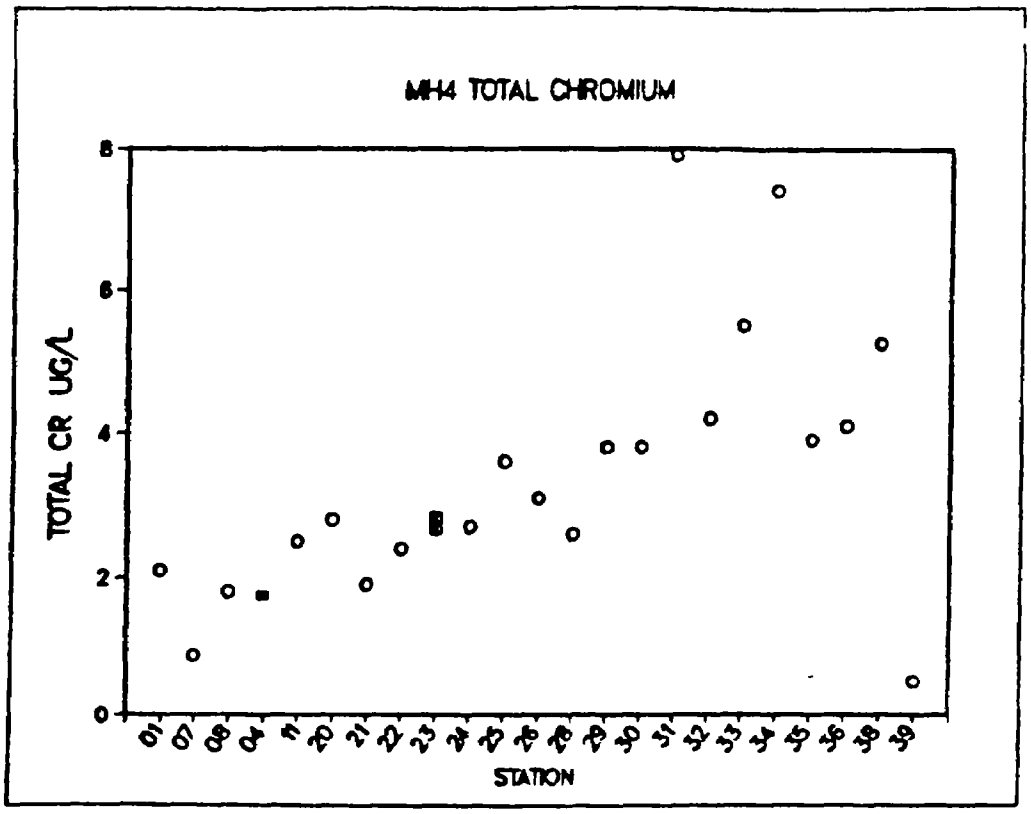


Figure 4.20. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 3. (See map, Figure 2.3).



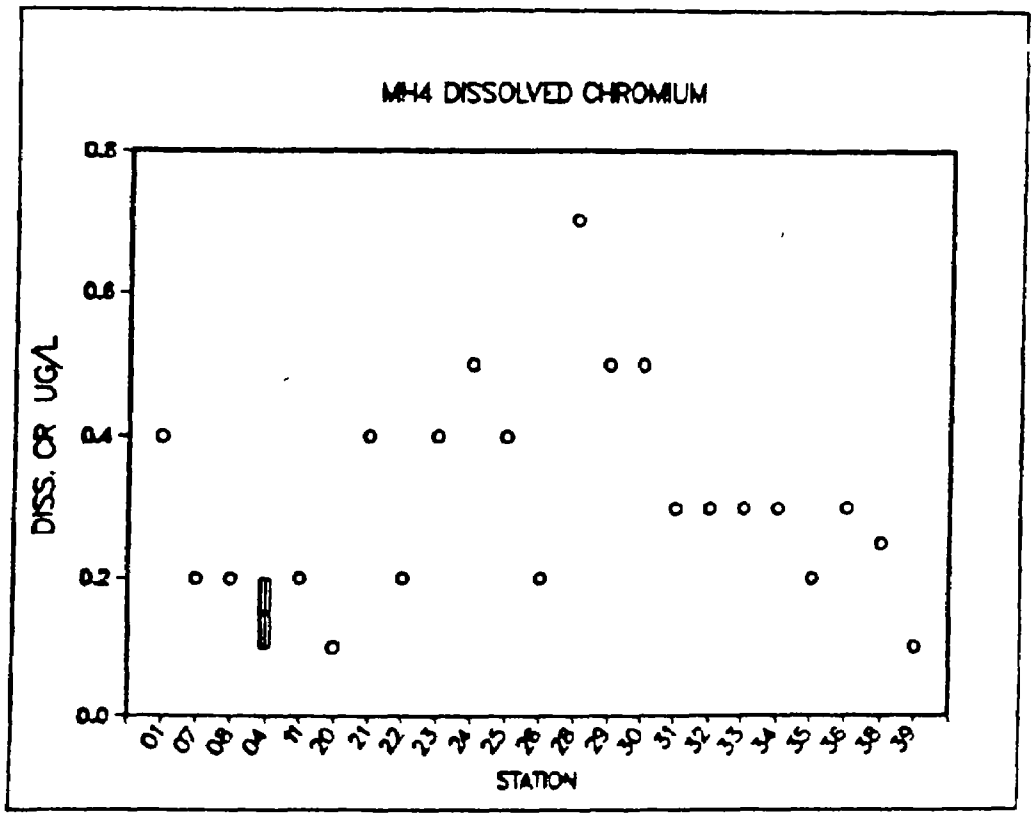
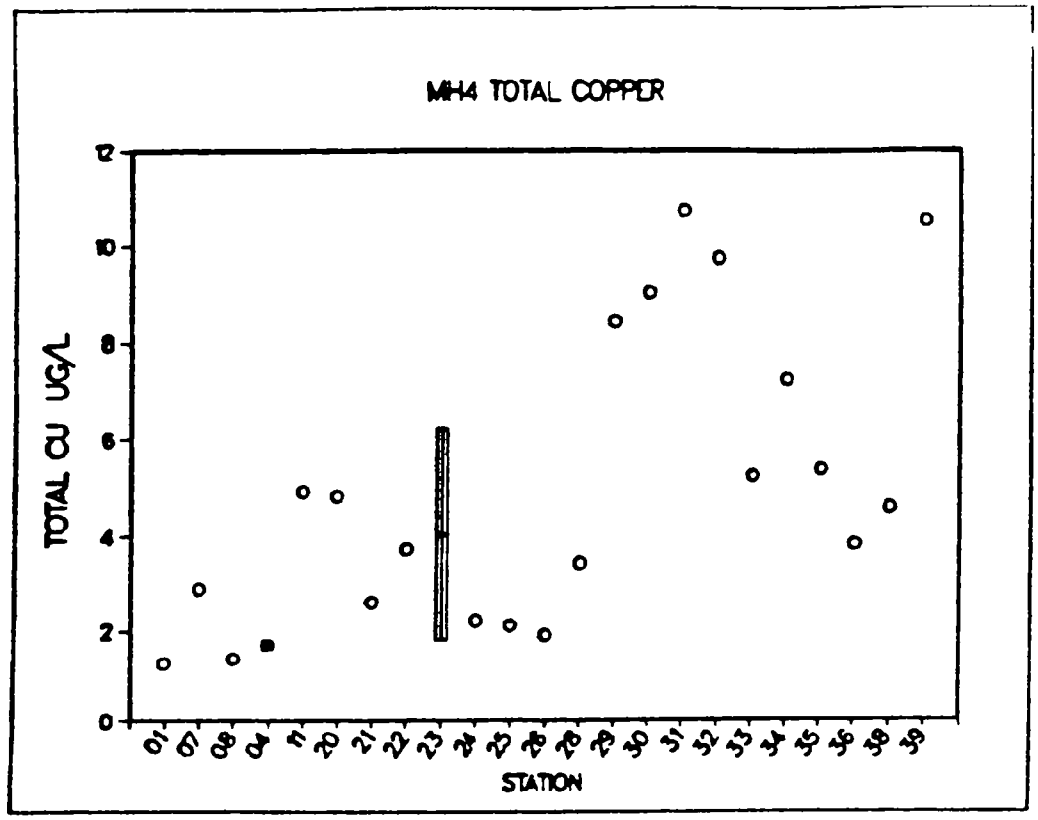


Figure 4.21. Spatial profile of total and dissolved chromium in grab and composite water samples. Monroe Harbor, Survey 4. (See map, Figure 2.4).



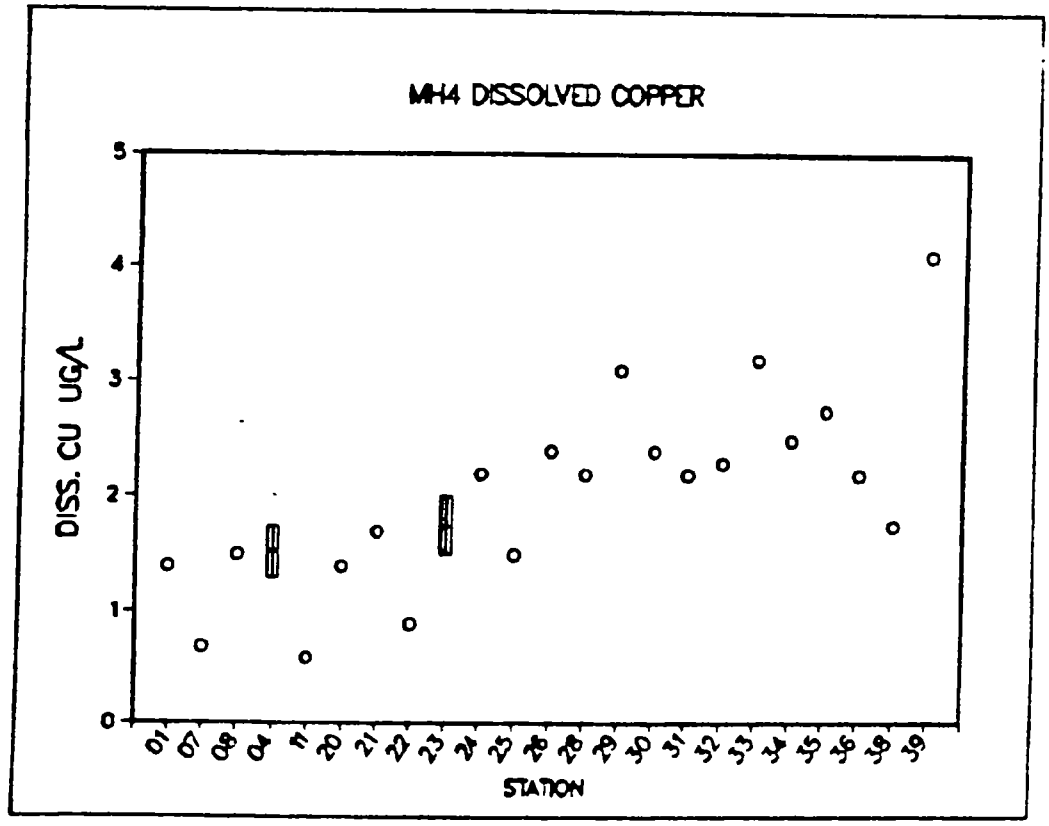
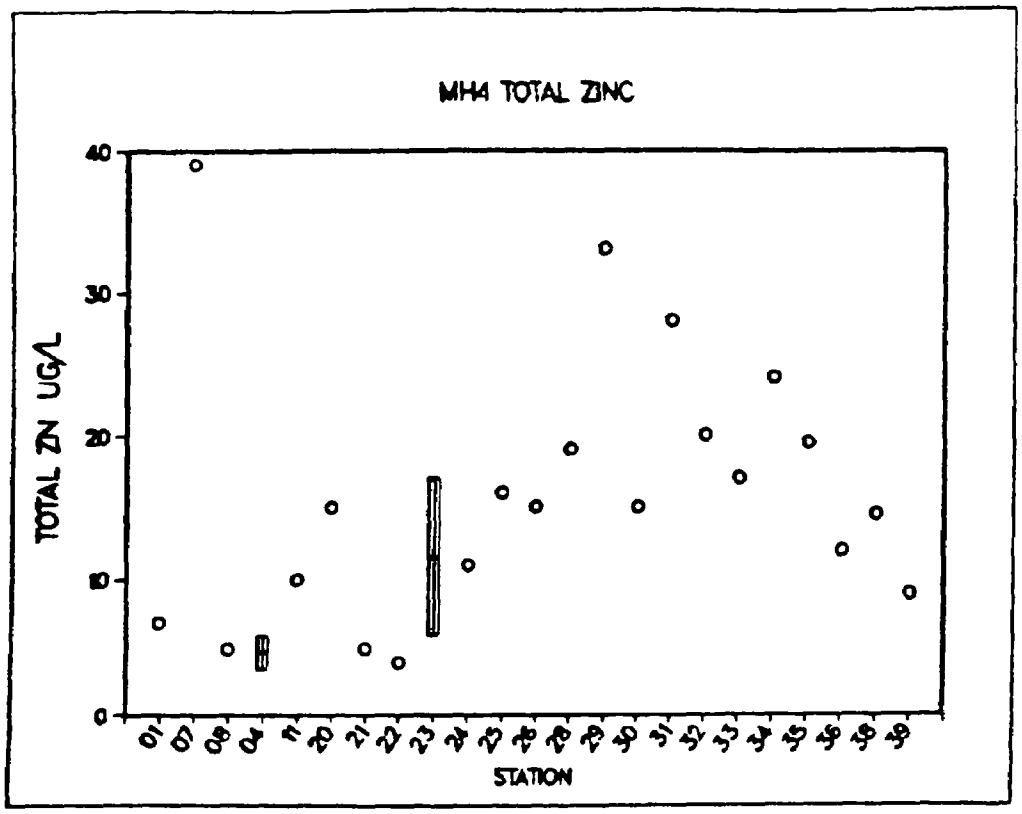


Figure 4.22. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 4. (See map, Figure 2.4).



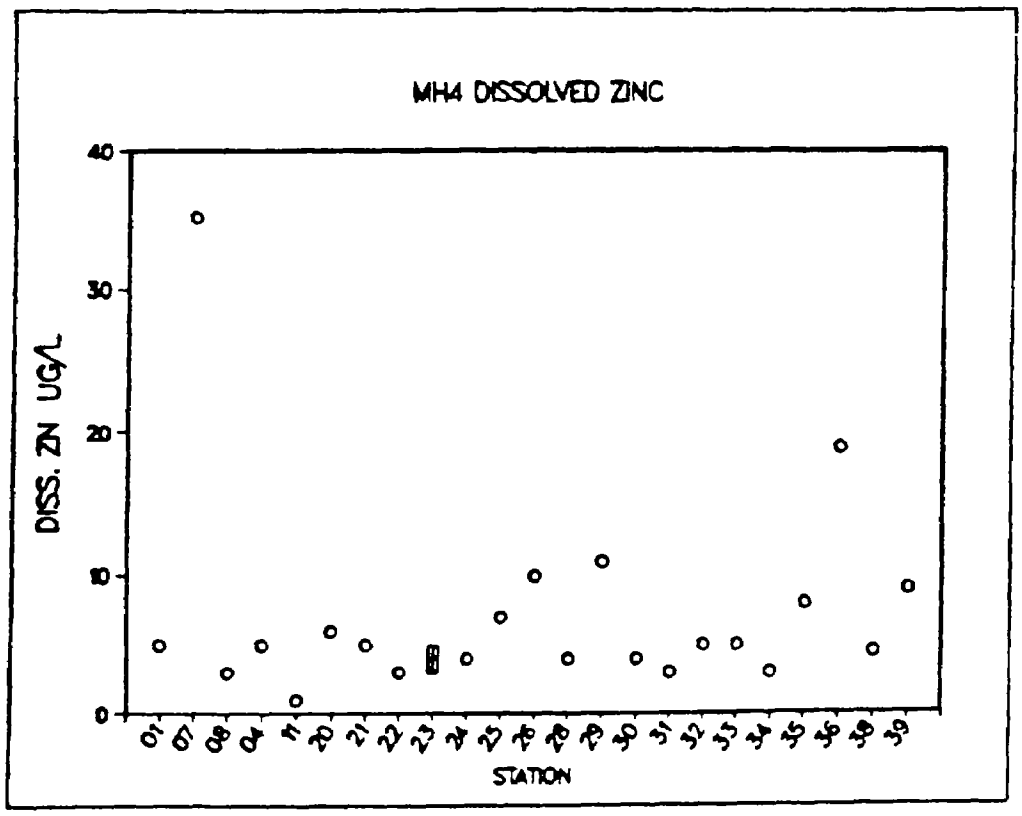
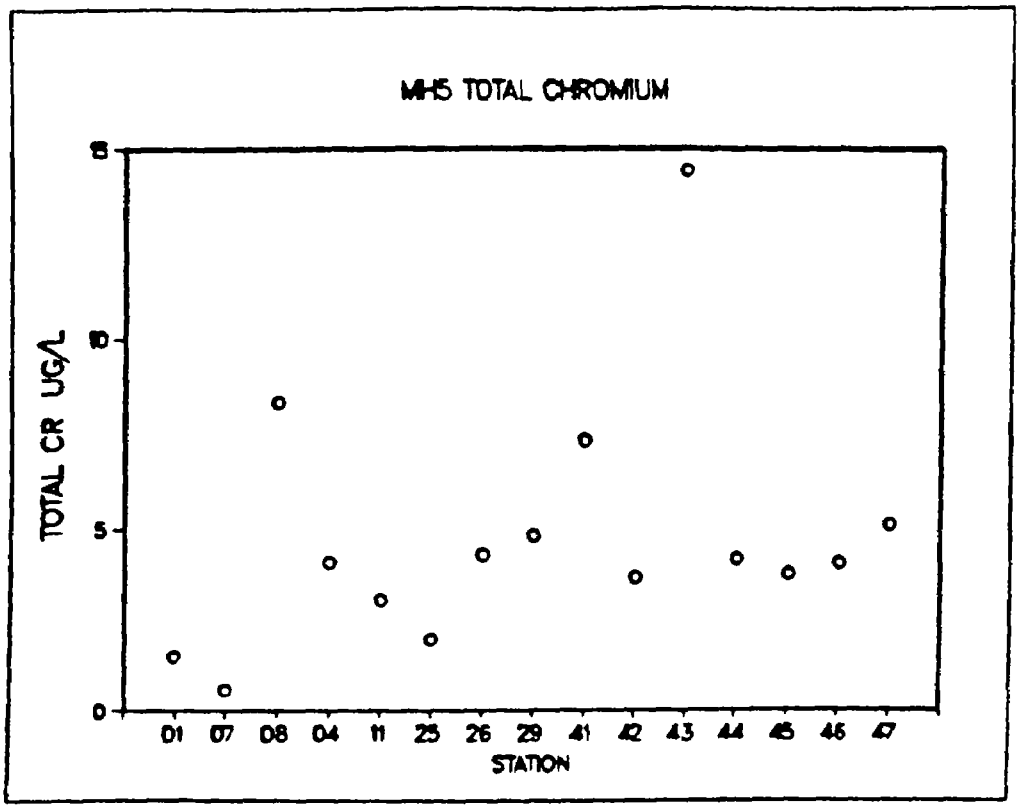


Figure 4.23. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 4. (See map, Figure 2.4).



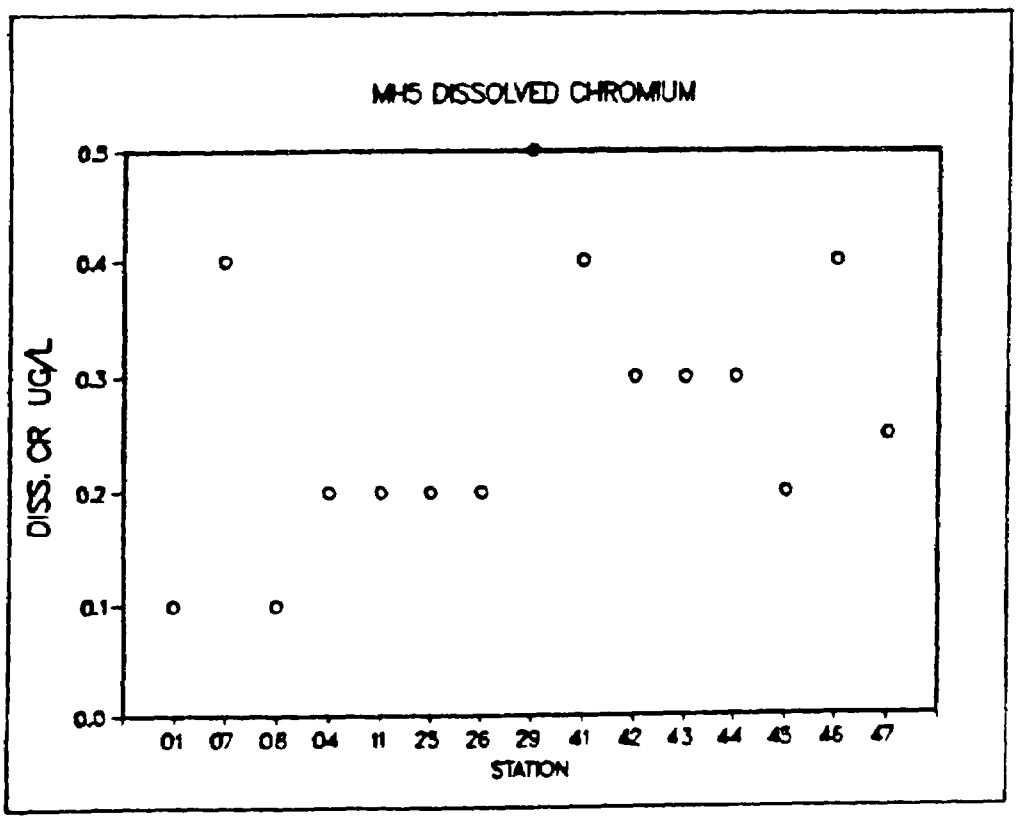
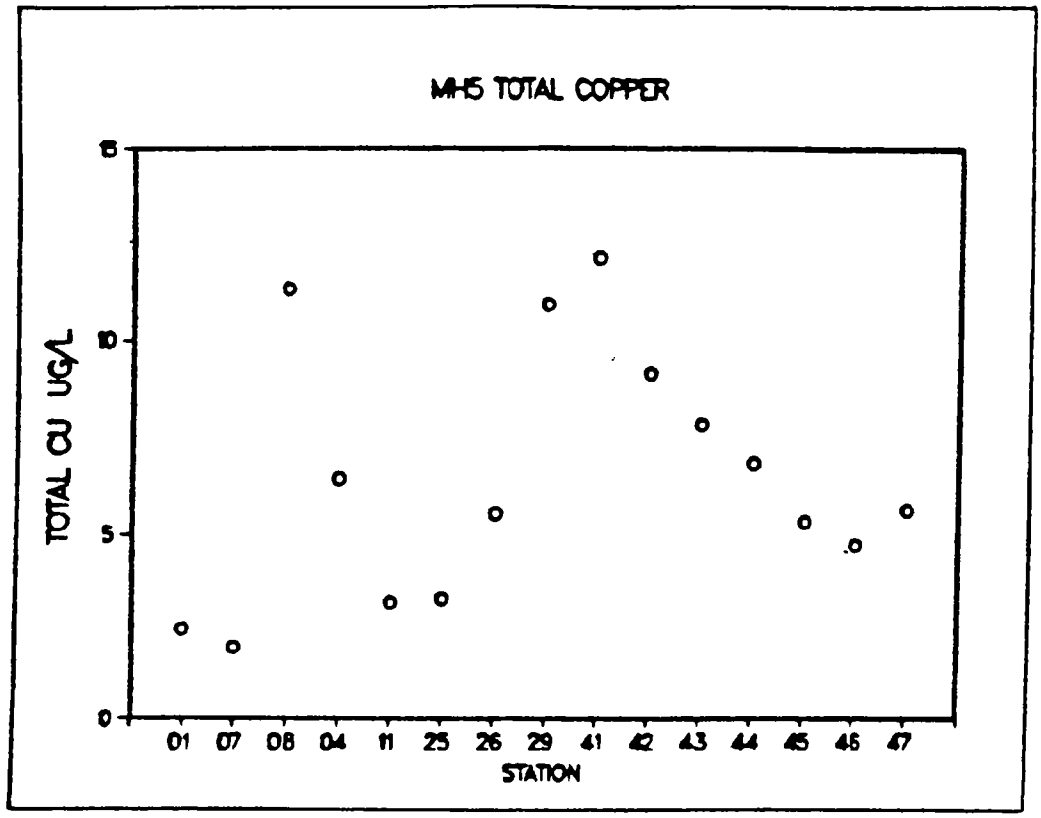


Figure 4.24. Spatial profile of total and dissolved chromiun in grab and composite water samples, Monroe Harbor, Survey 5. (See map, Figure 2.5).



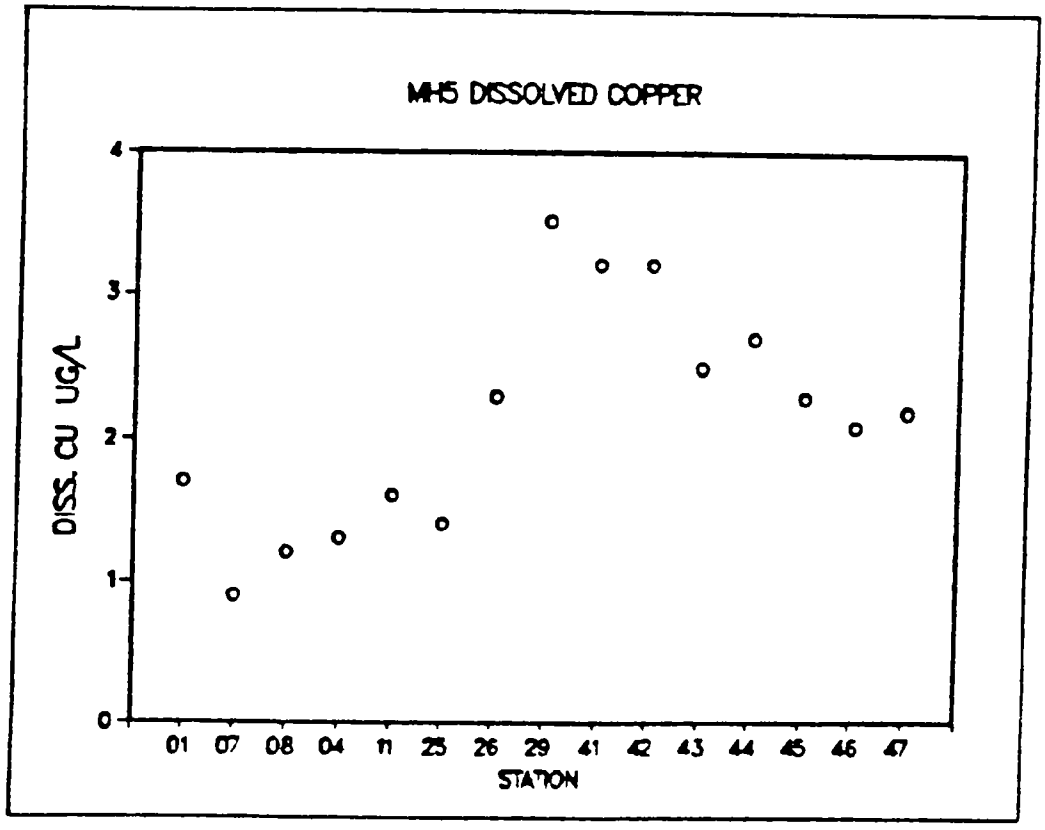
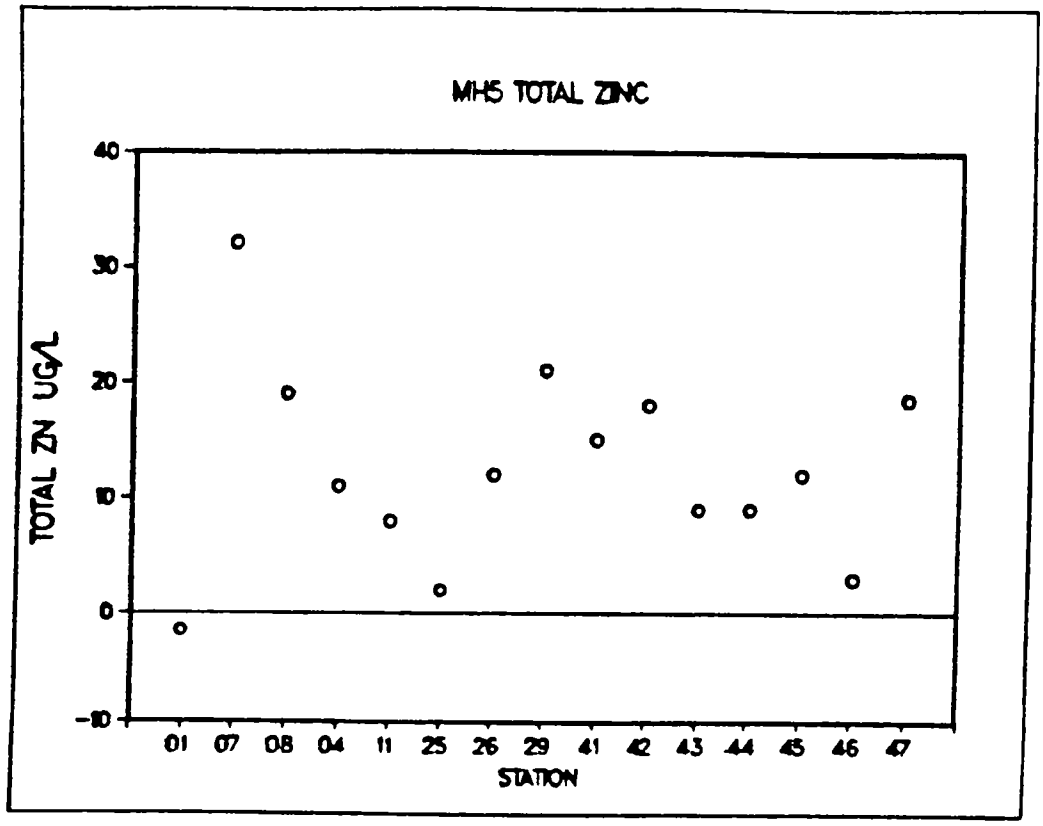


Figure 4.25. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 5. (See map, Figure 2.5).



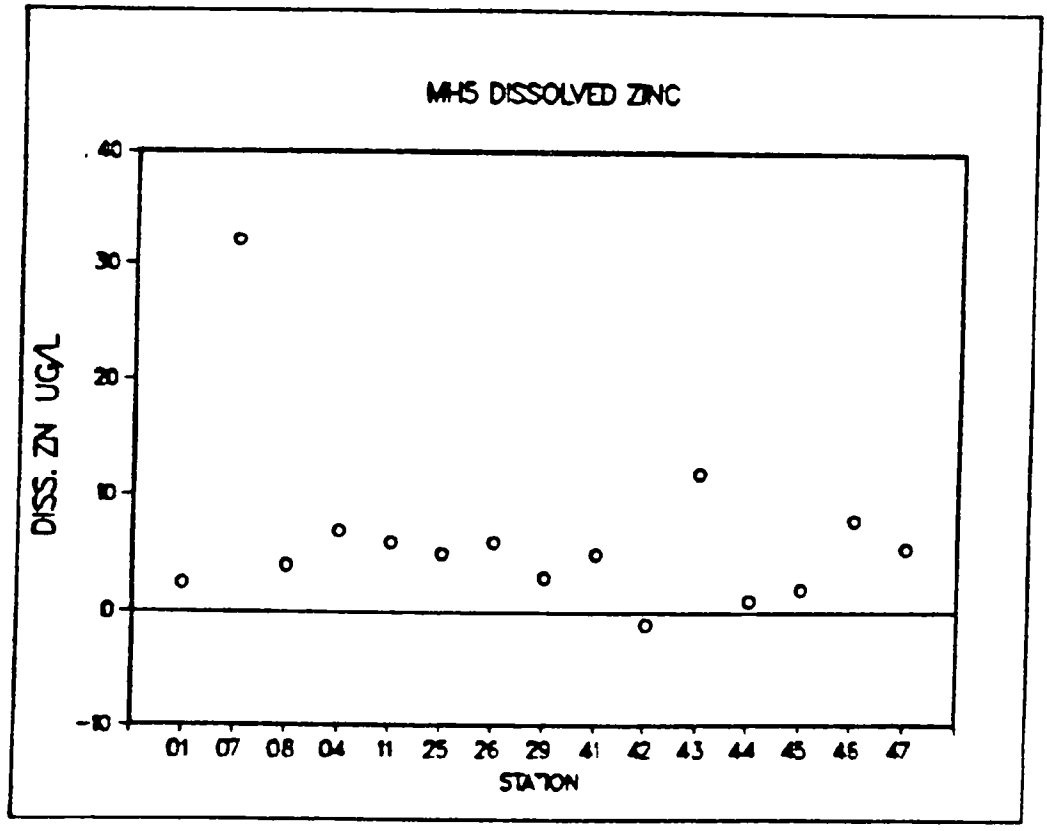
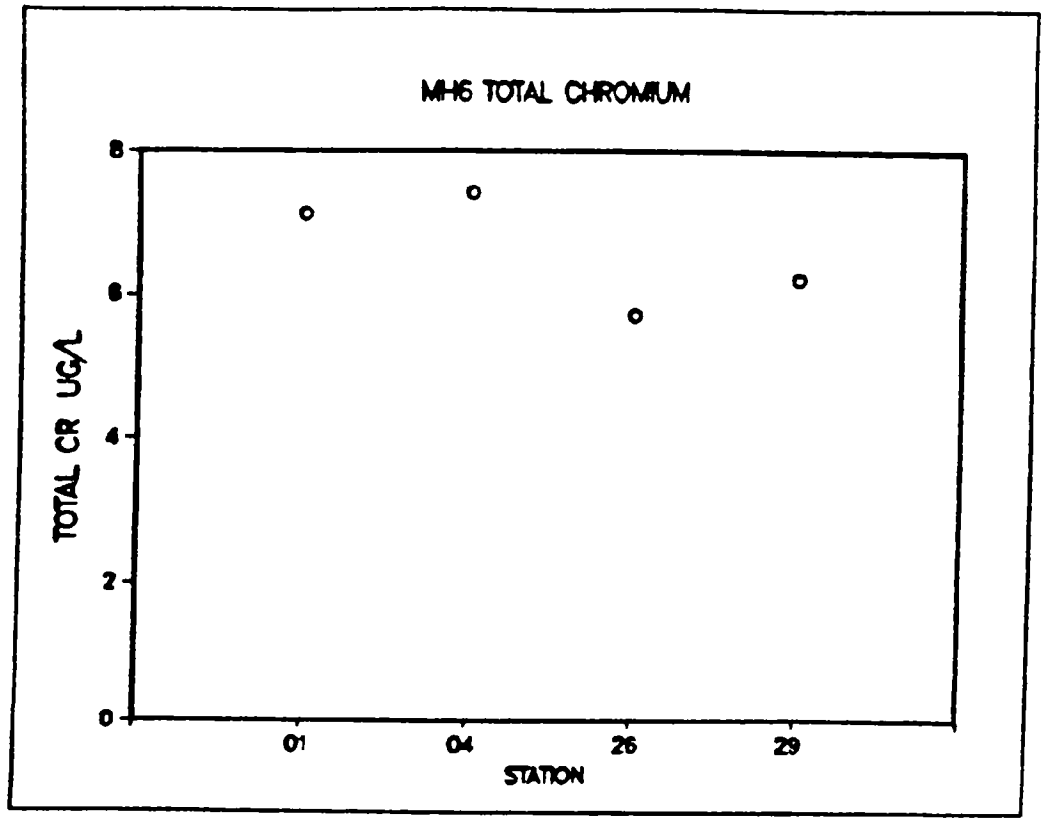


Figure 4.26. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 5. (See map, Figure 2.5).



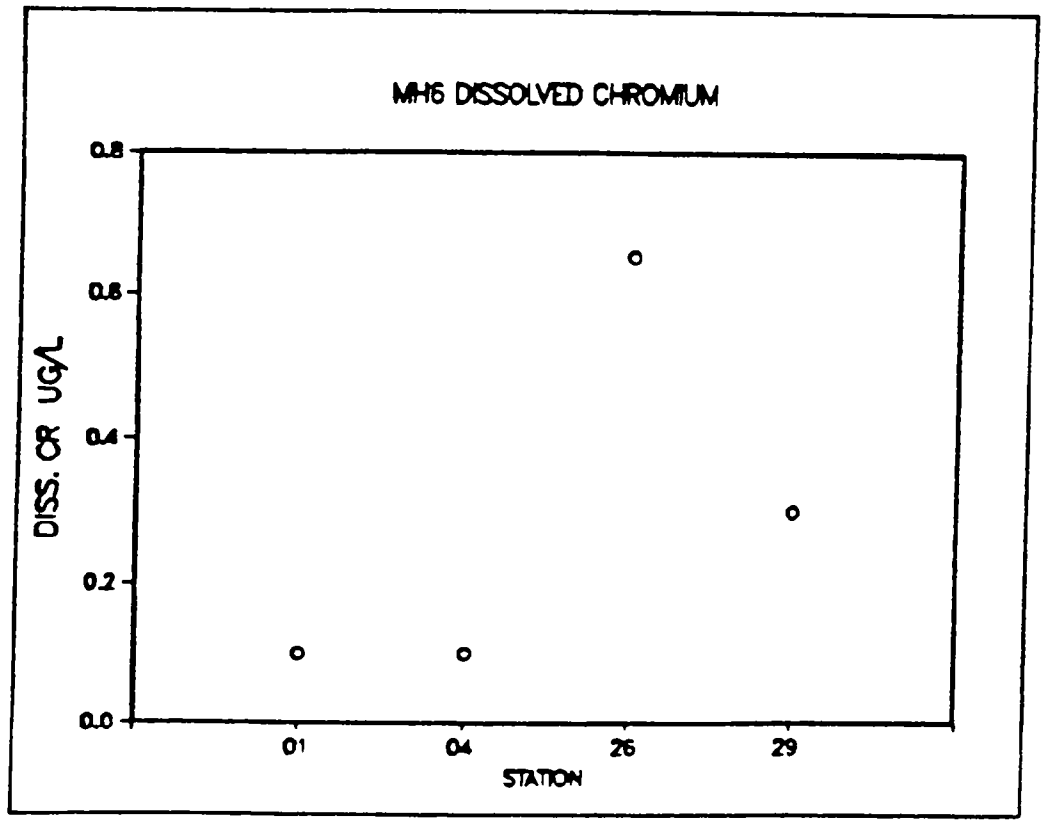
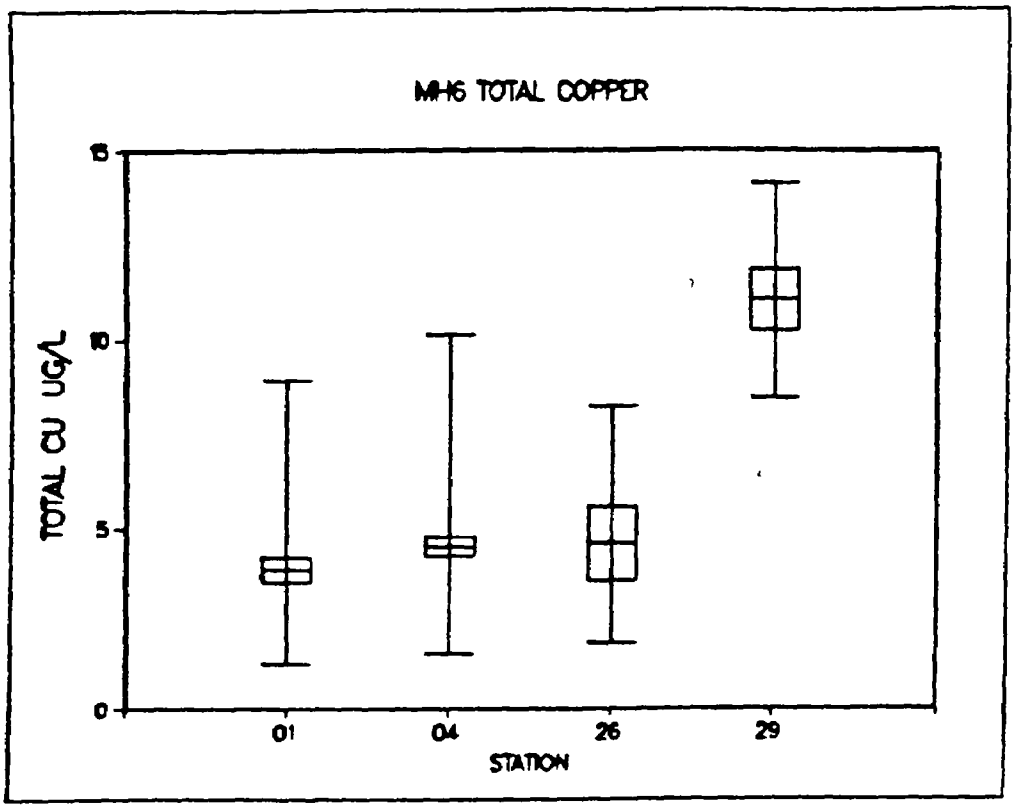


Figure 4.27. Spatial profile of total and dissolved chromium in grab and composite water samples. Monroe Harbor, Survey 6. (See map, Figure 2.6).



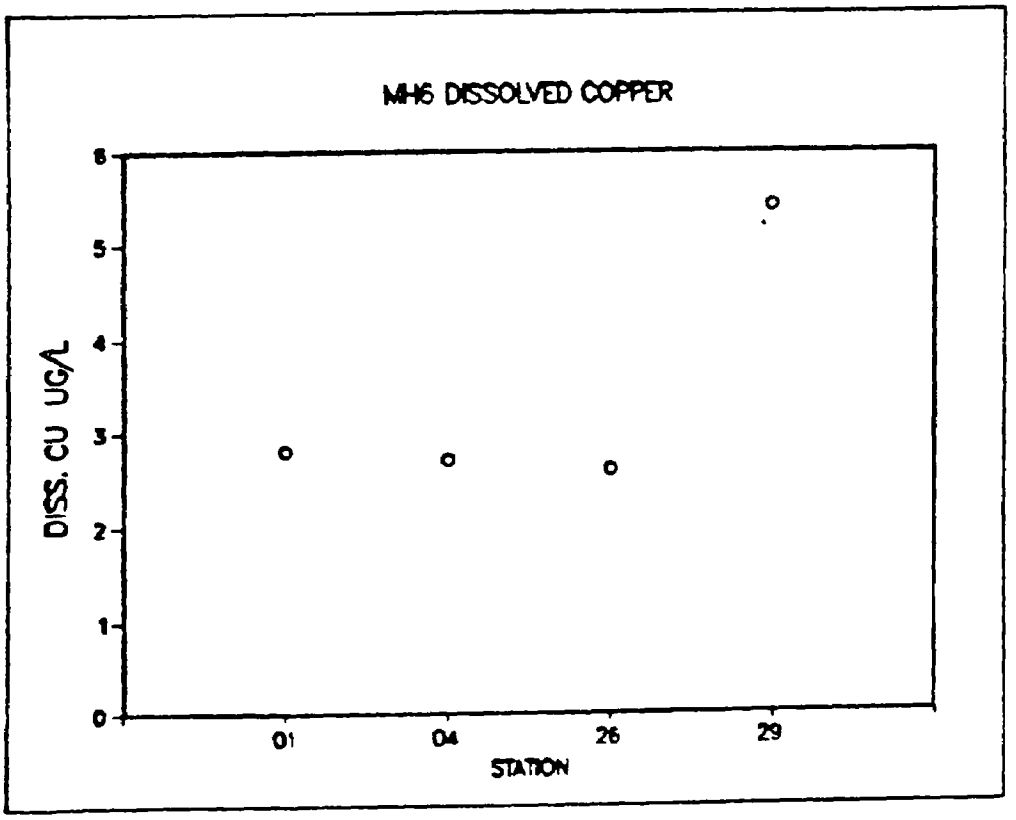
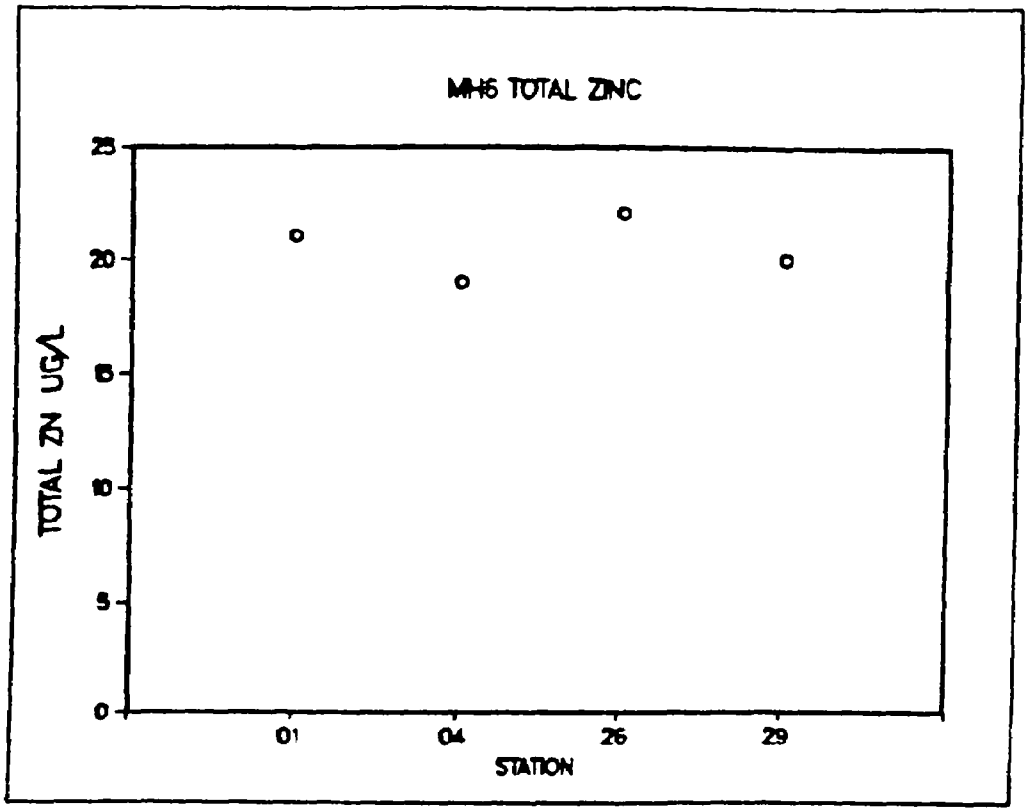


Figure 4.28. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 6. (See map, Figure 2.6).



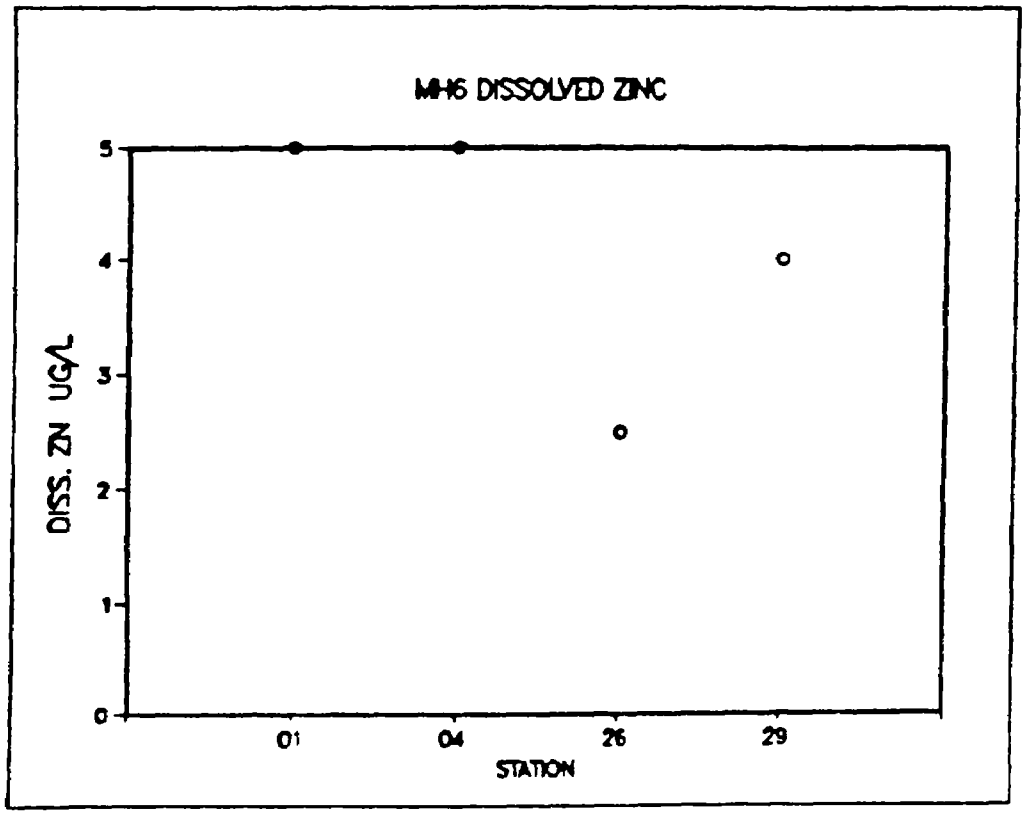
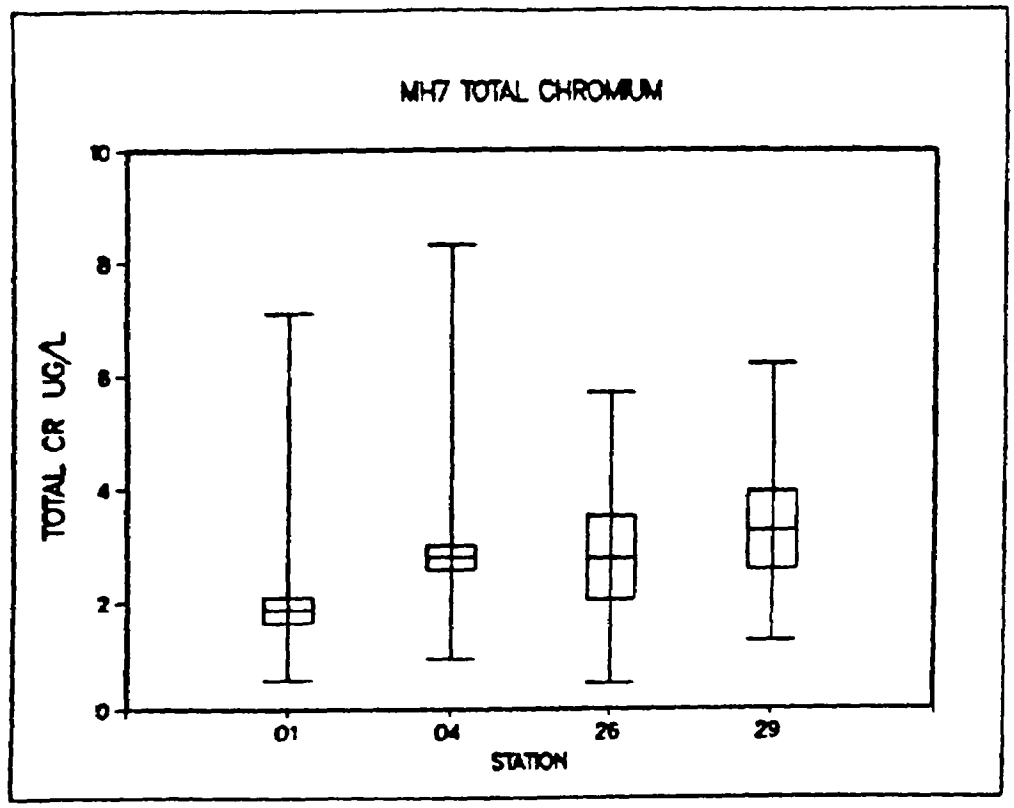


Figure 4.29. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 6. (See map, Figure 2.6).



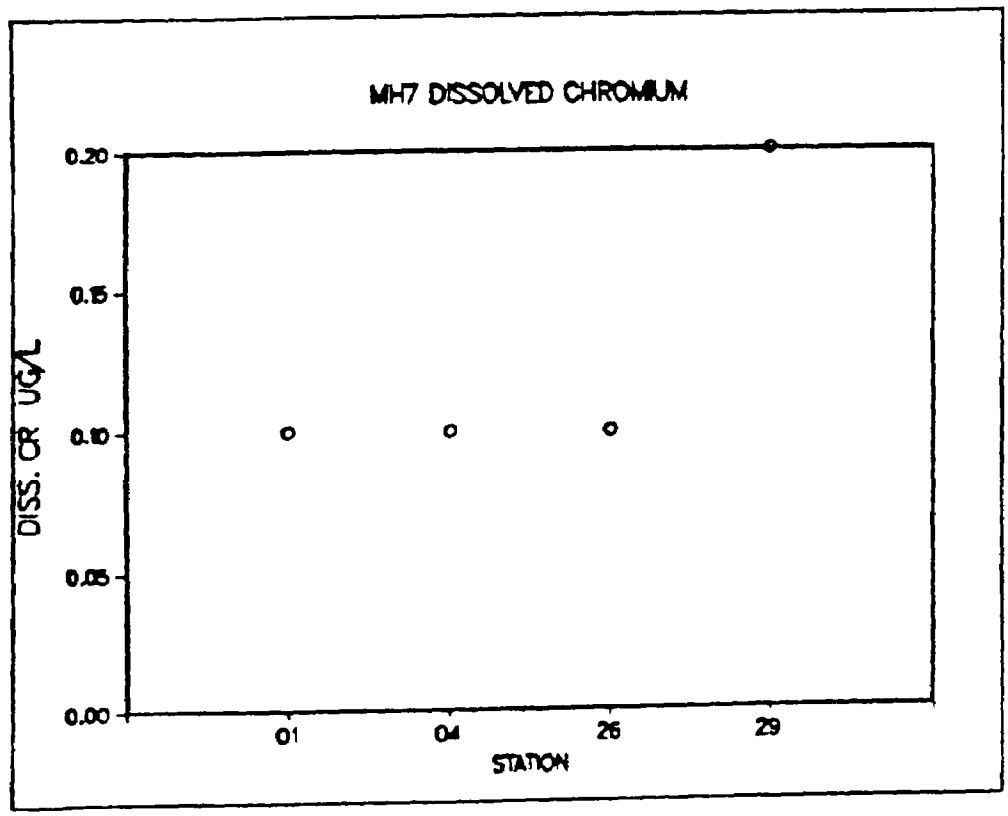
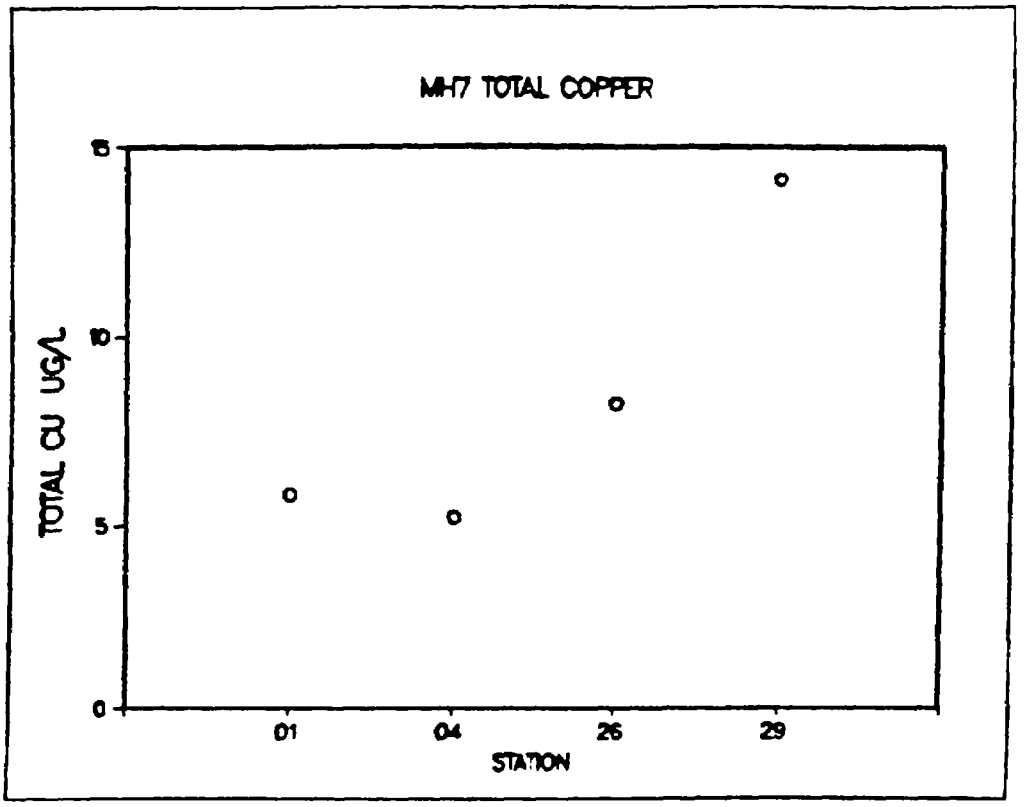


Figure 4.30. Spatial profile of total and dissolved chromium in grab and composite water samples. Monroe Harbor, Survey 7. (See map, Figure 2.6).



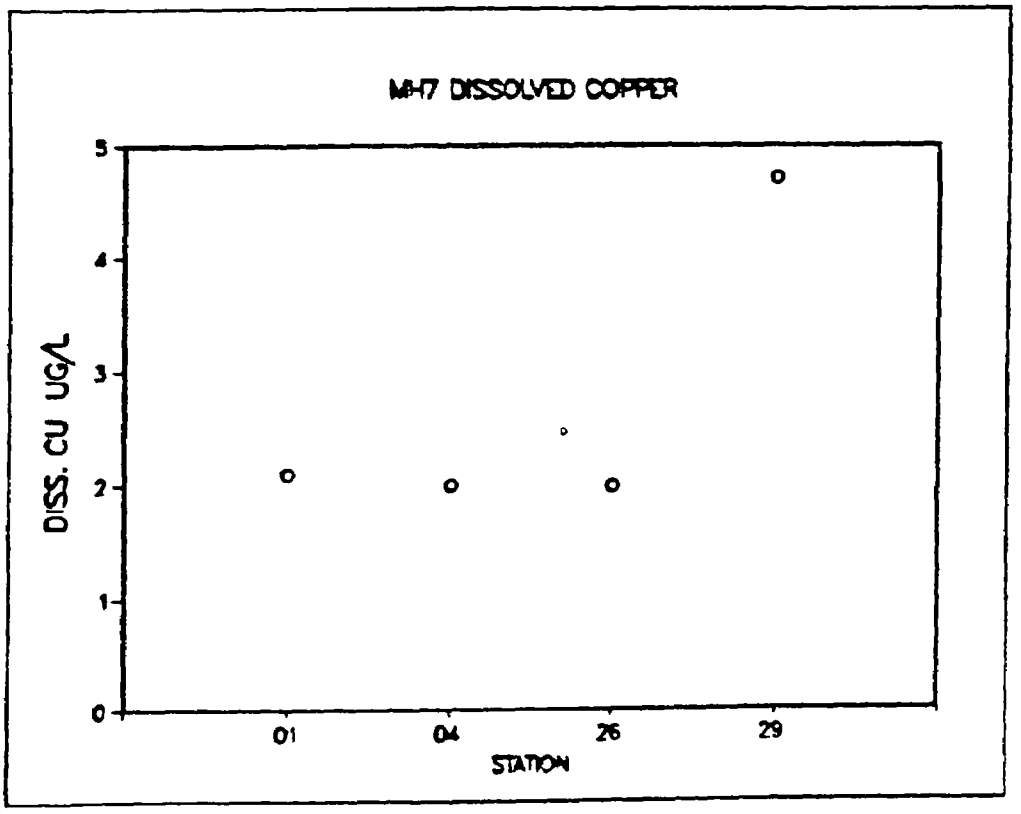
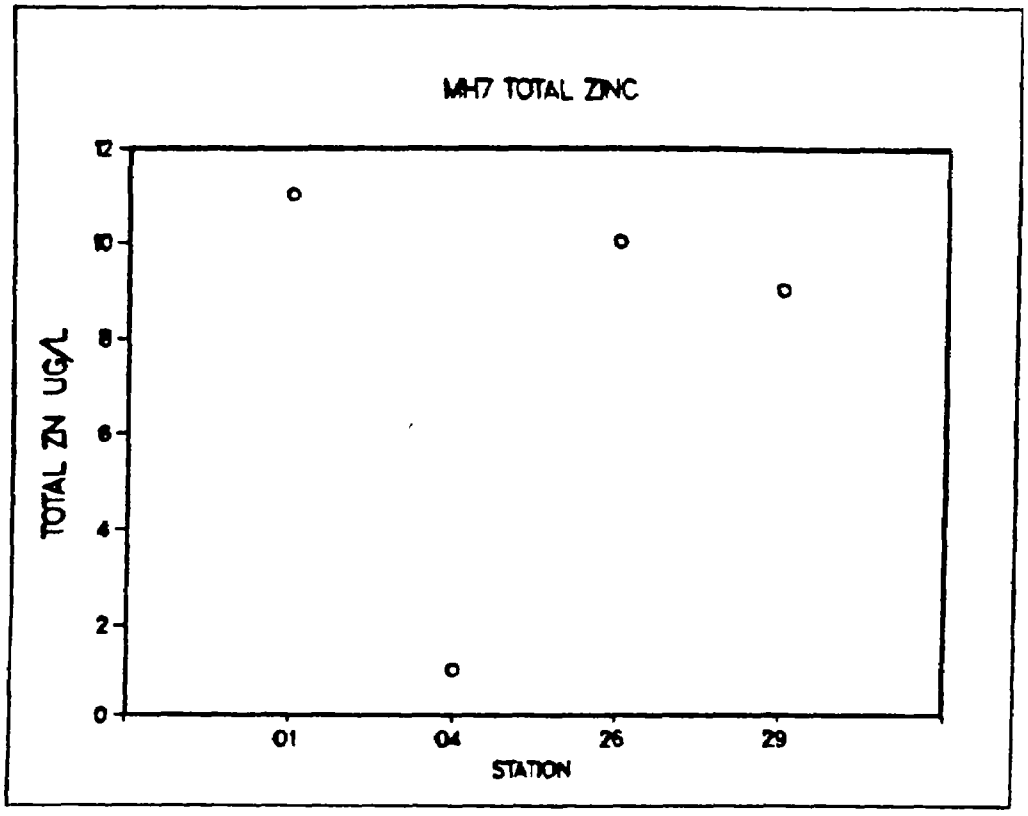


Figure 4.31. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 7. (See map, Figure 2.6).



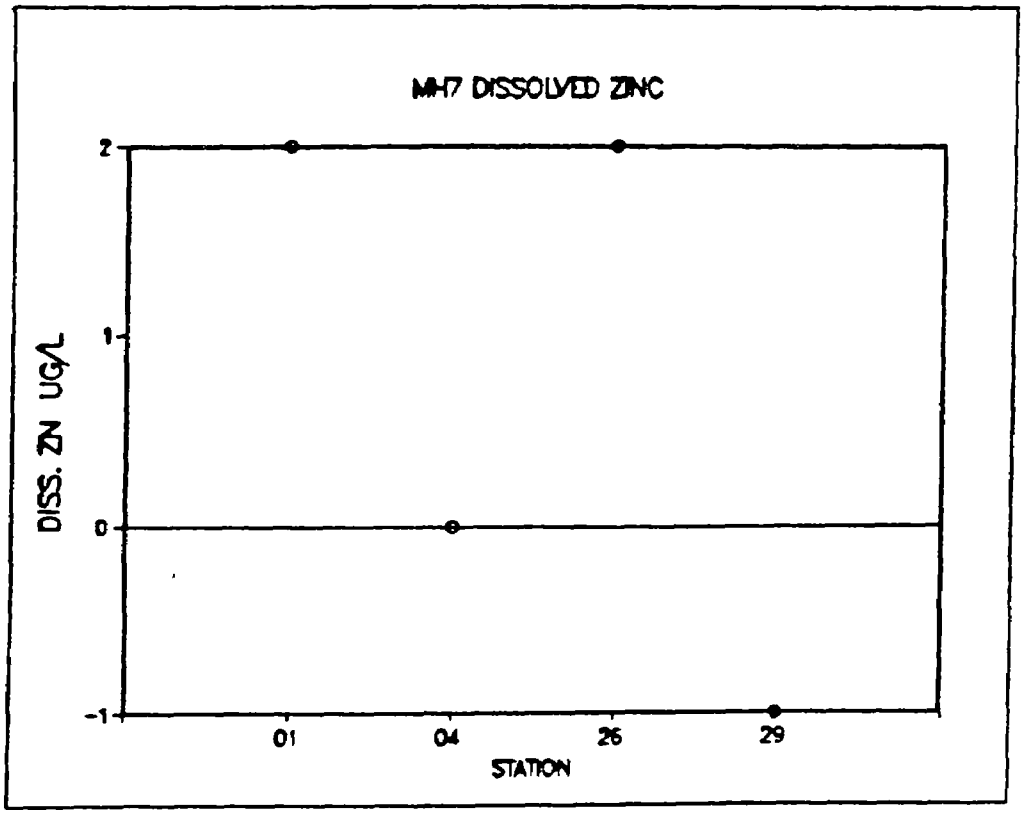
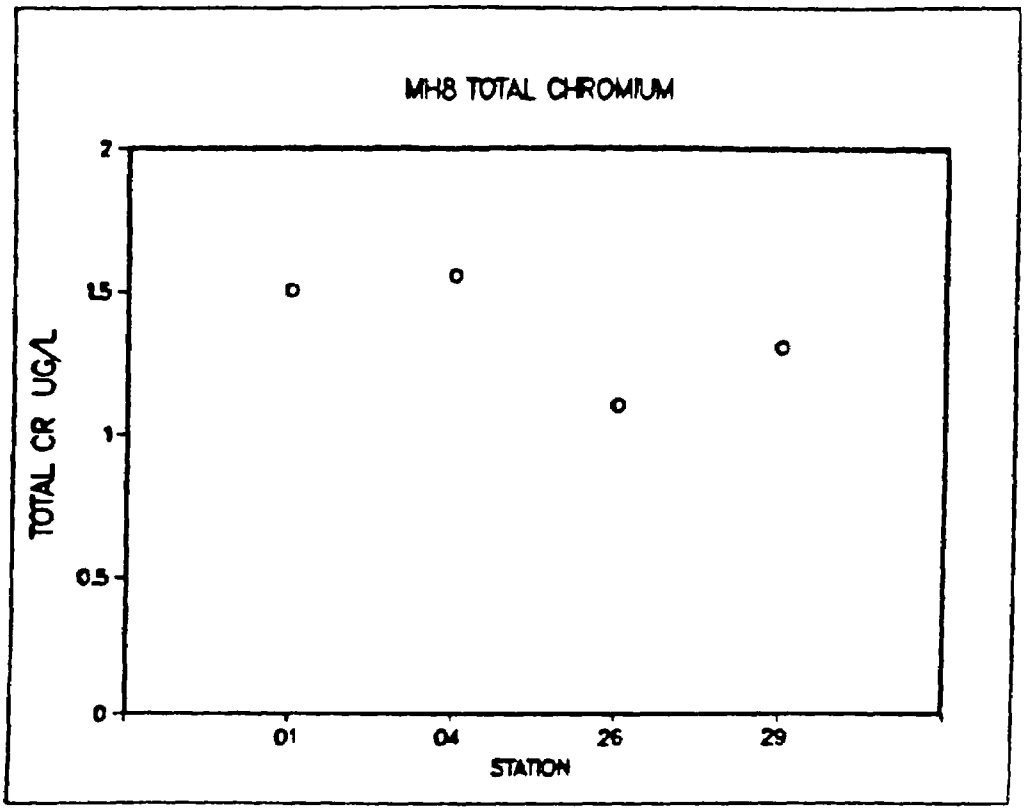


Figure 4.32. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 7. (See map, Figure 2.6).



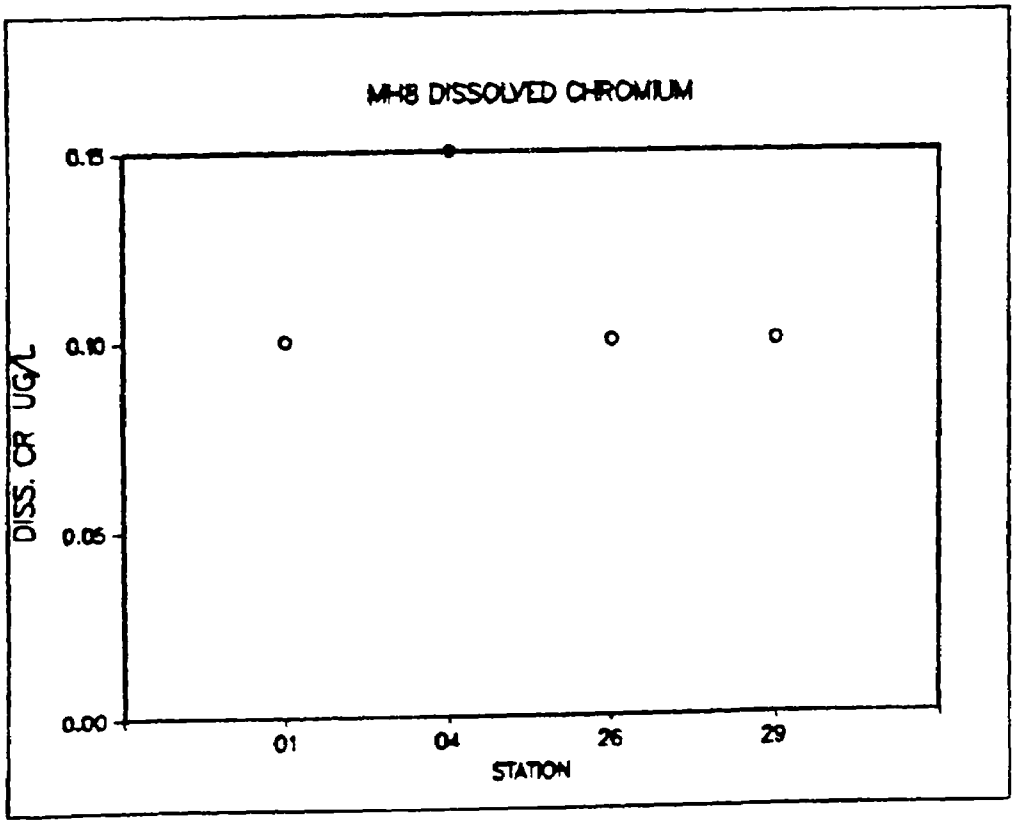
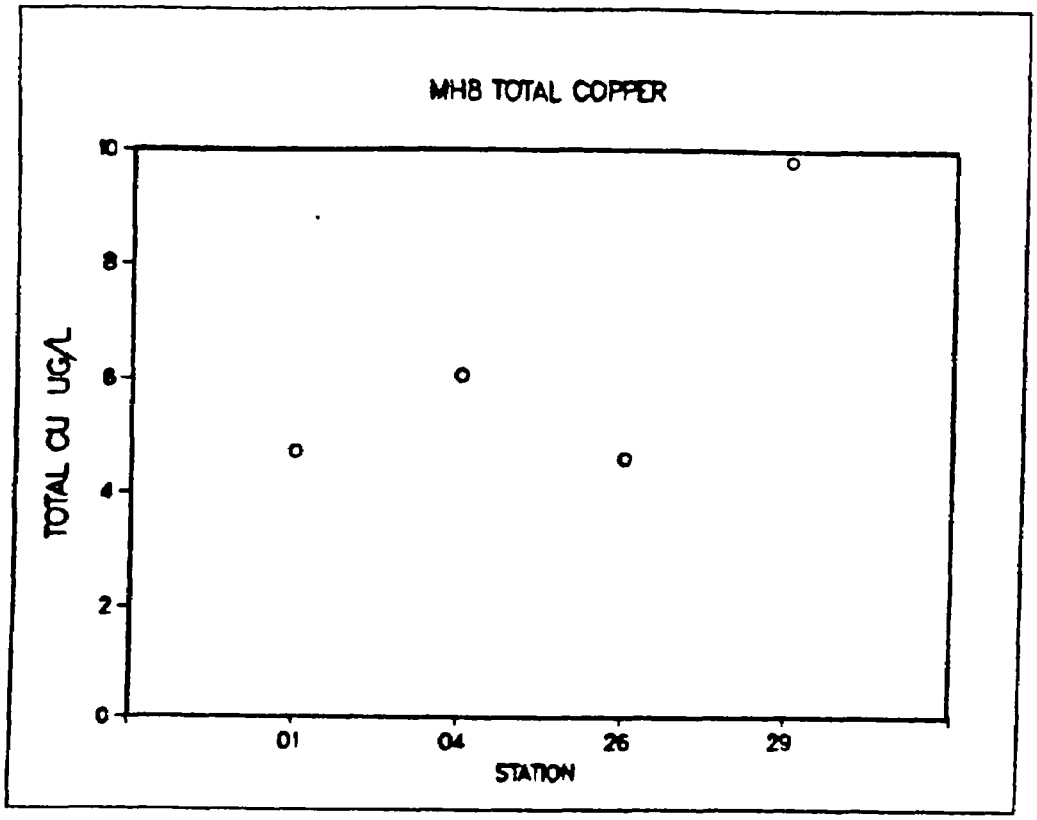


Figure 4.33. Spatial profile of total and dissolved chromium in grab and composite water samples. Monroe Harbor, Survey 8. (See map, Figure 2.6).



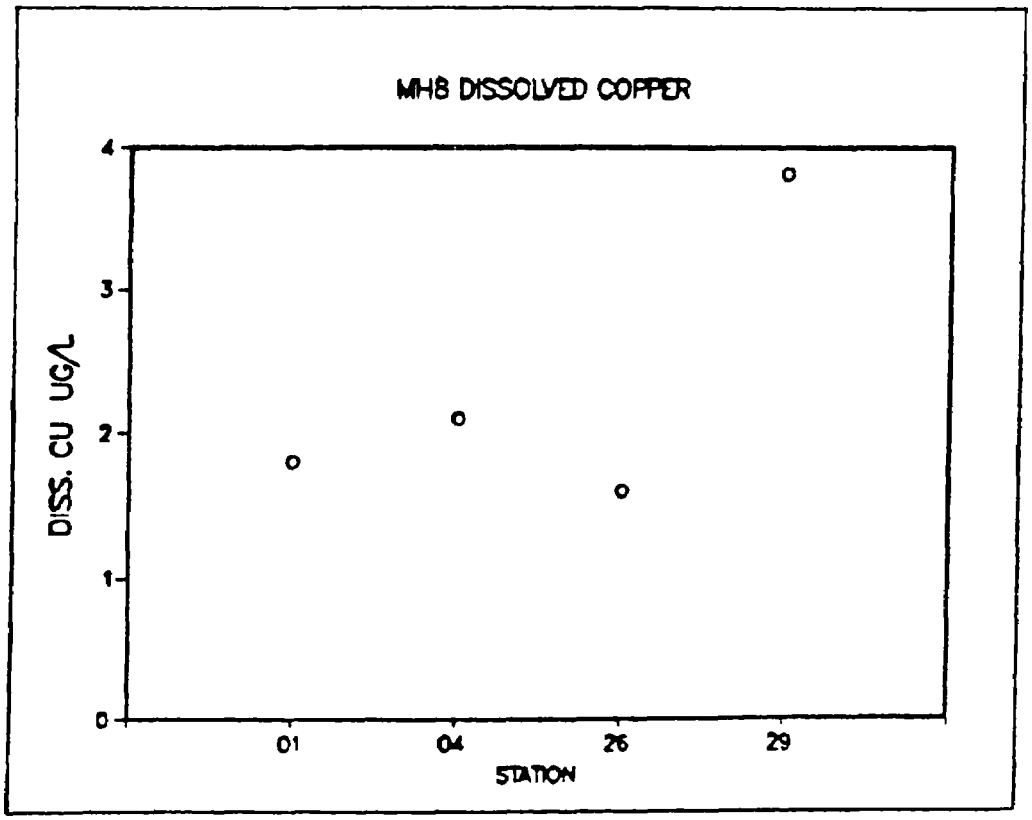
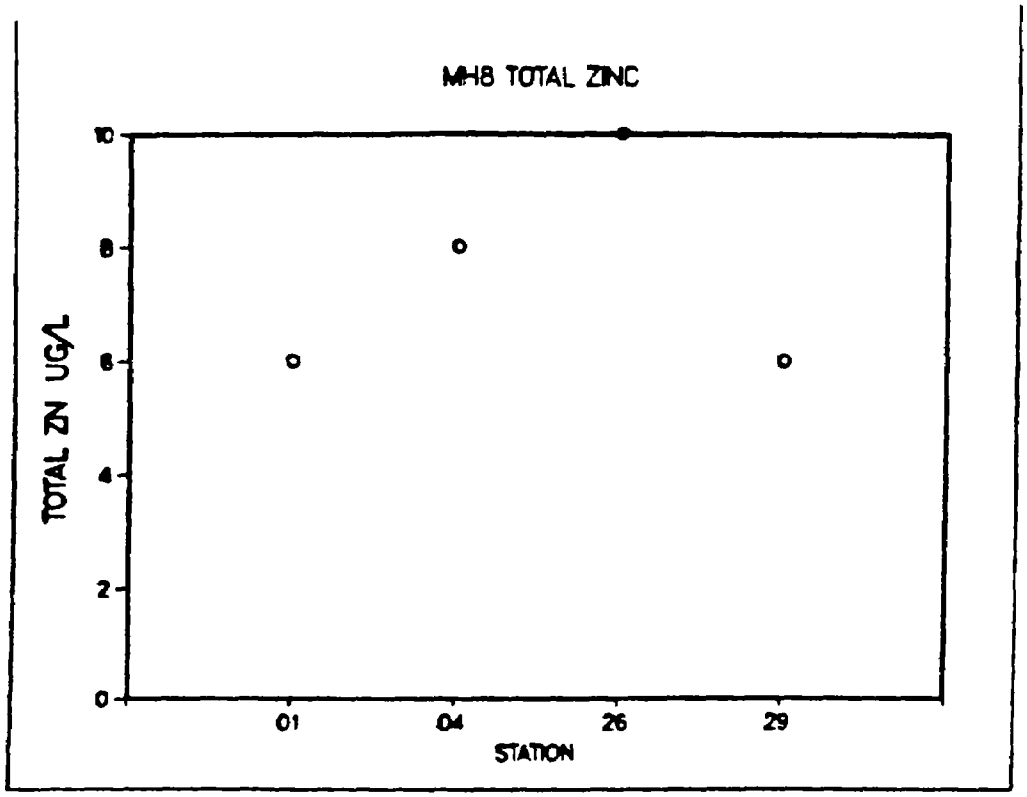


Figure 4.34. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 8. (See map, Figure 2.6).



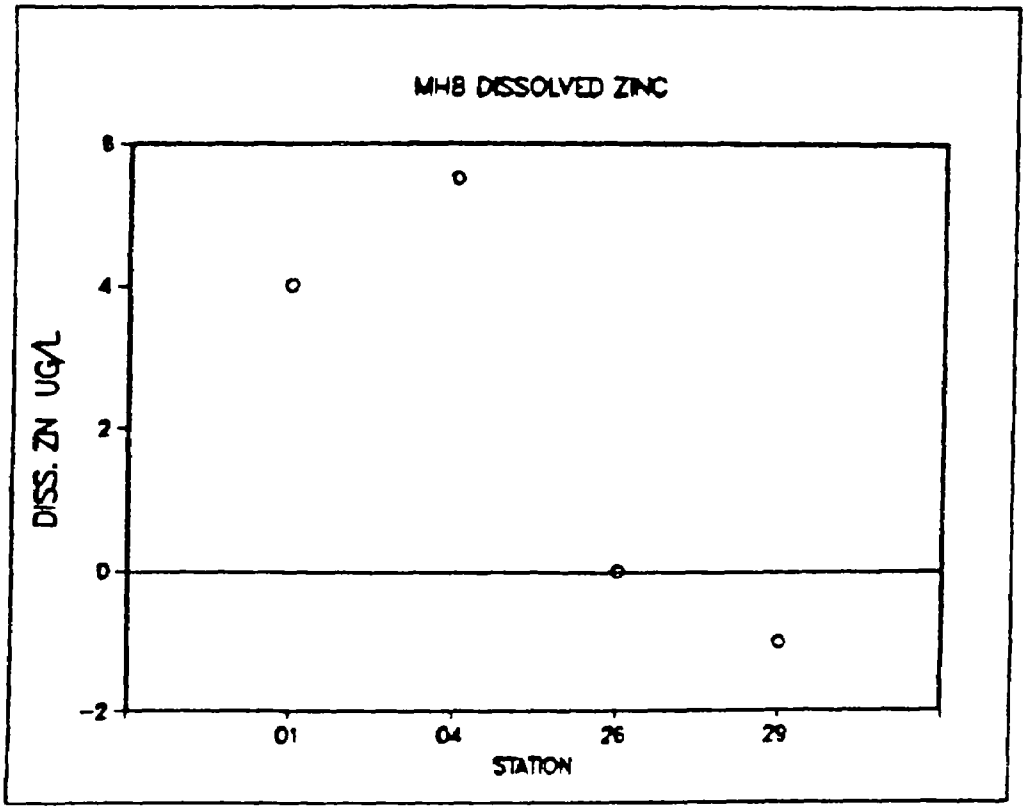
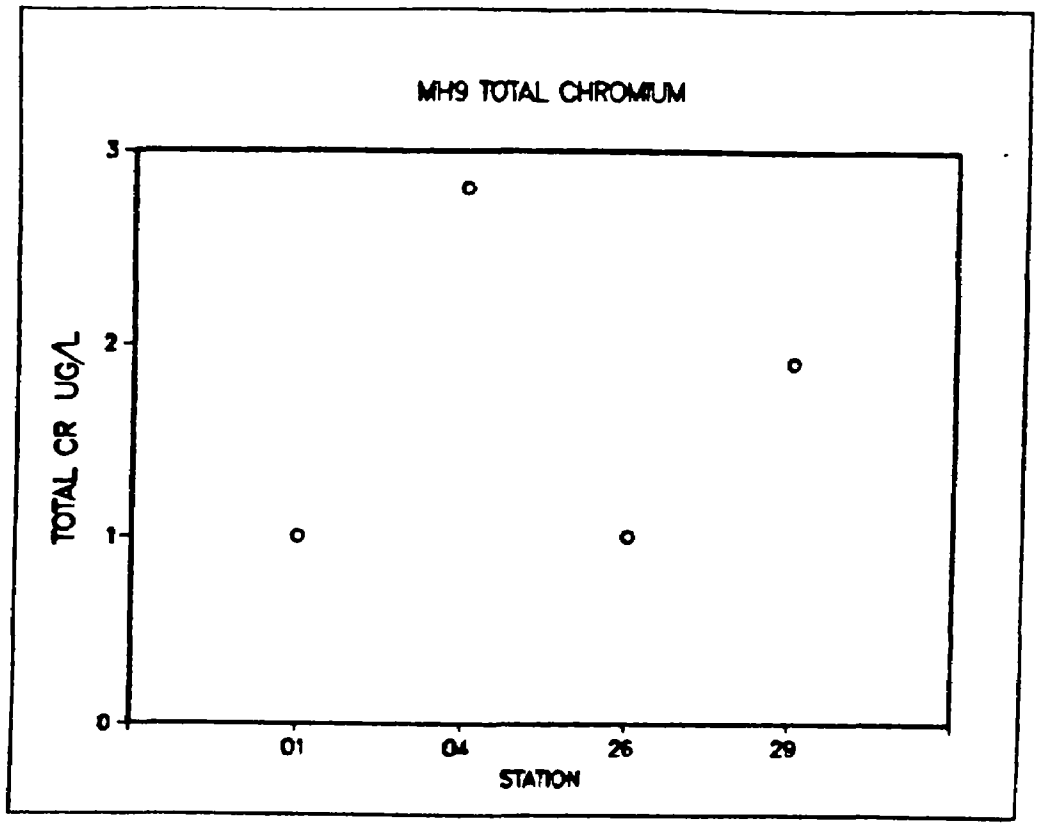


Figure 4.35. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 8. (See map, Figure 2.6).



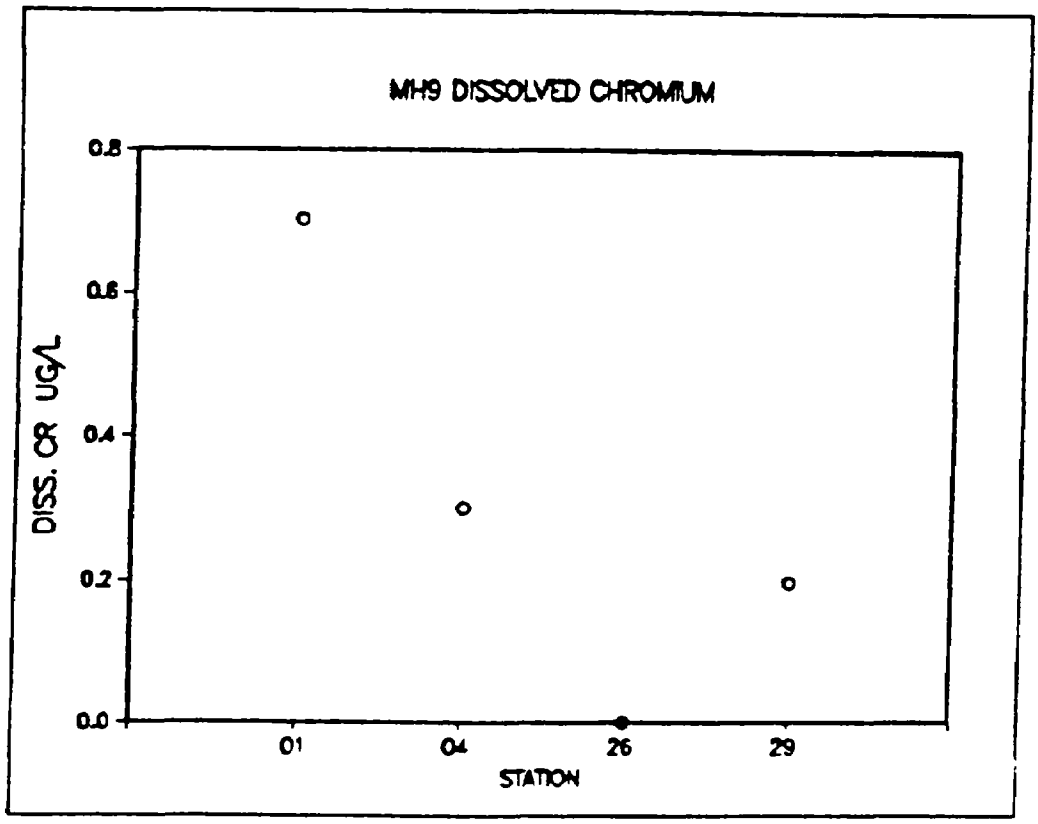
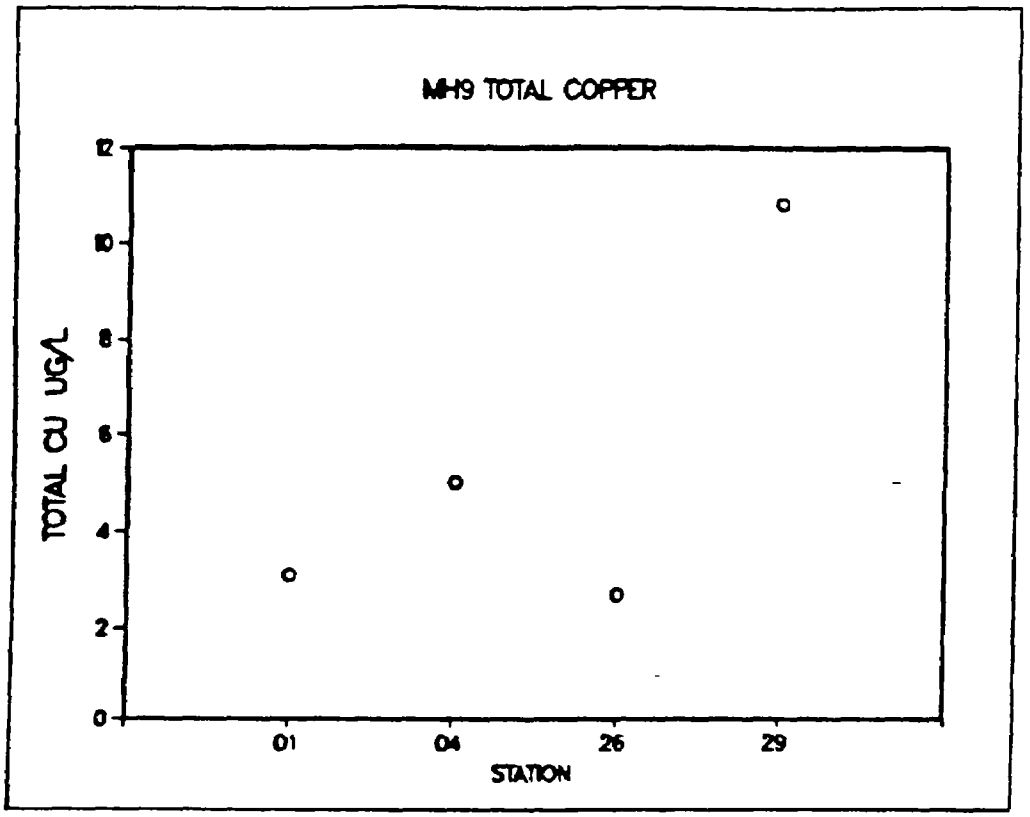


Figure 4.36. Spatial profile of total and dissolved chromium in grab and composite water samples. Monroe Harbor, Survey 9. (See map, Figure 2.6).



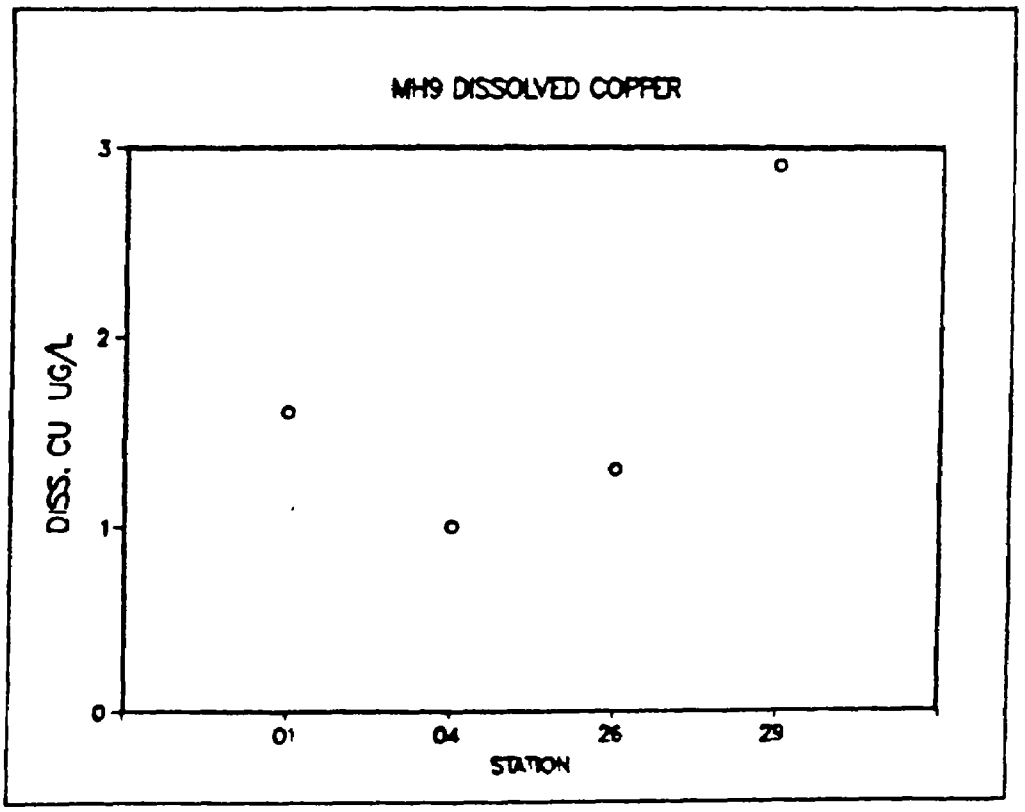
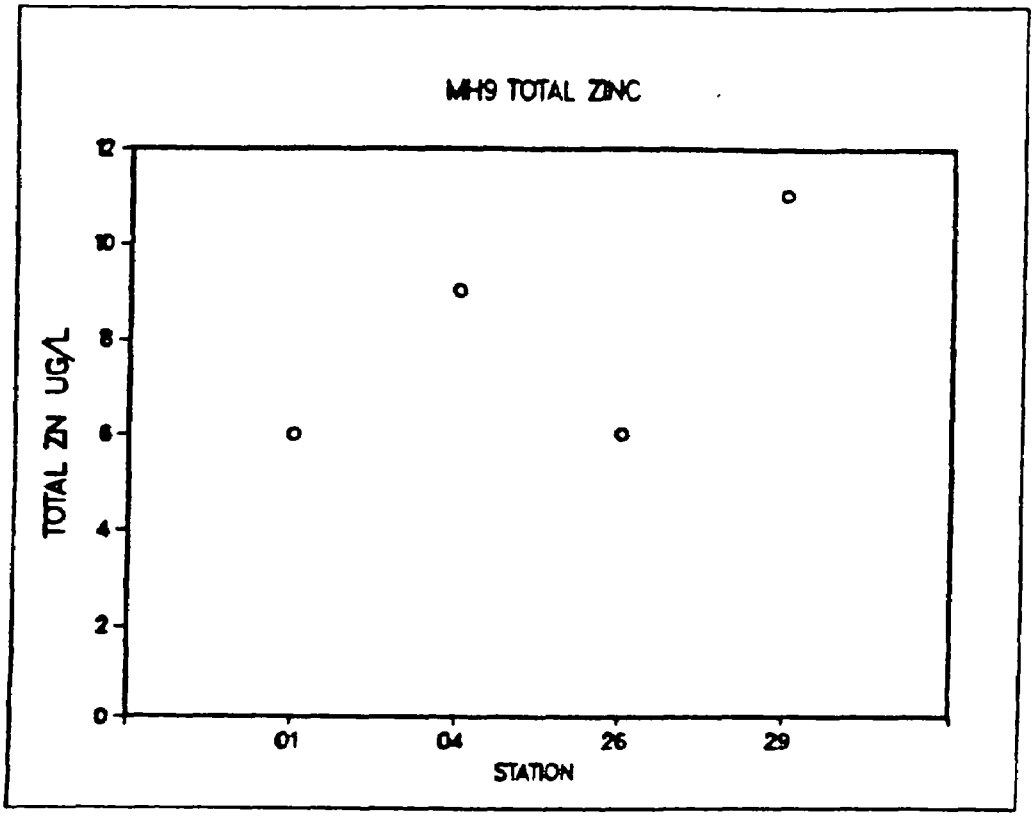


Figure 4.37. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 9. (See map, Figure 2.6).



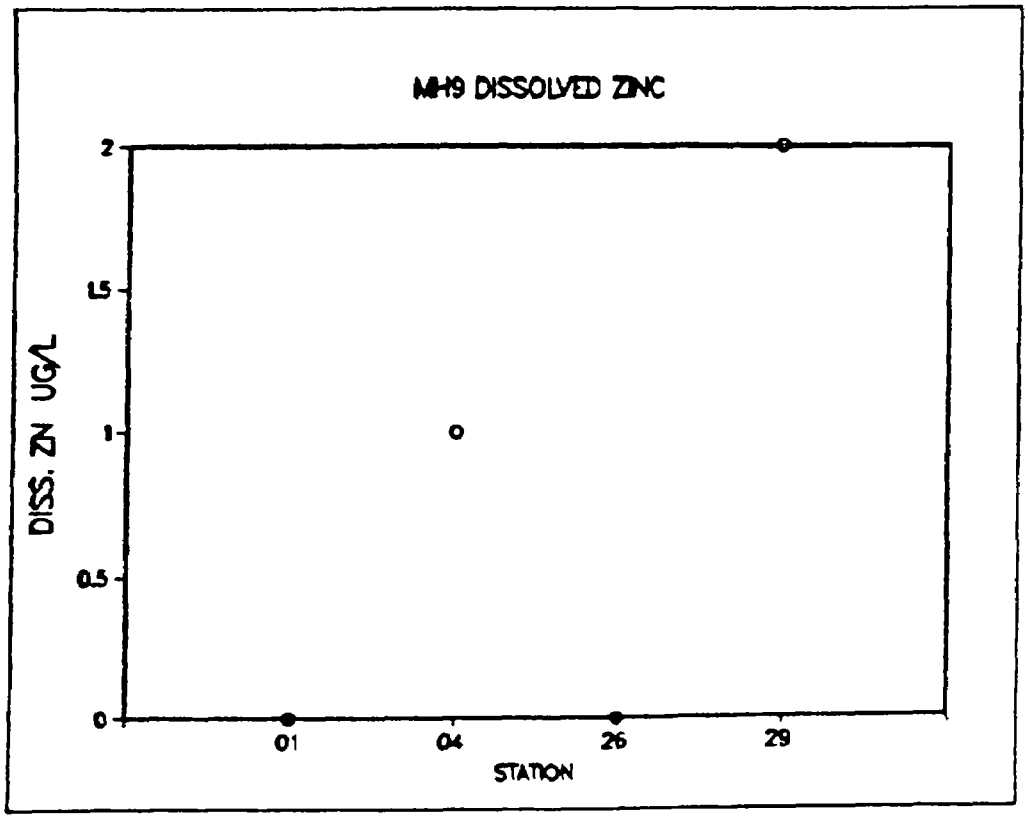
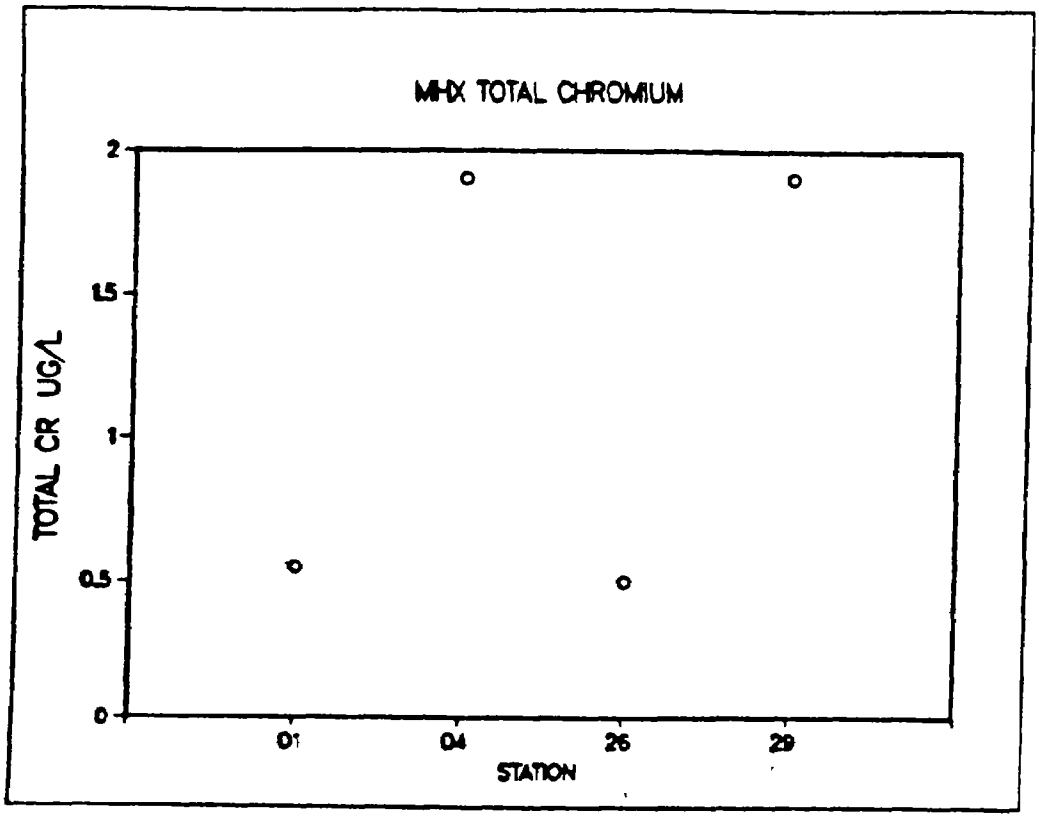


Figure 4.38. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 9. (See map, Figure 2.6).



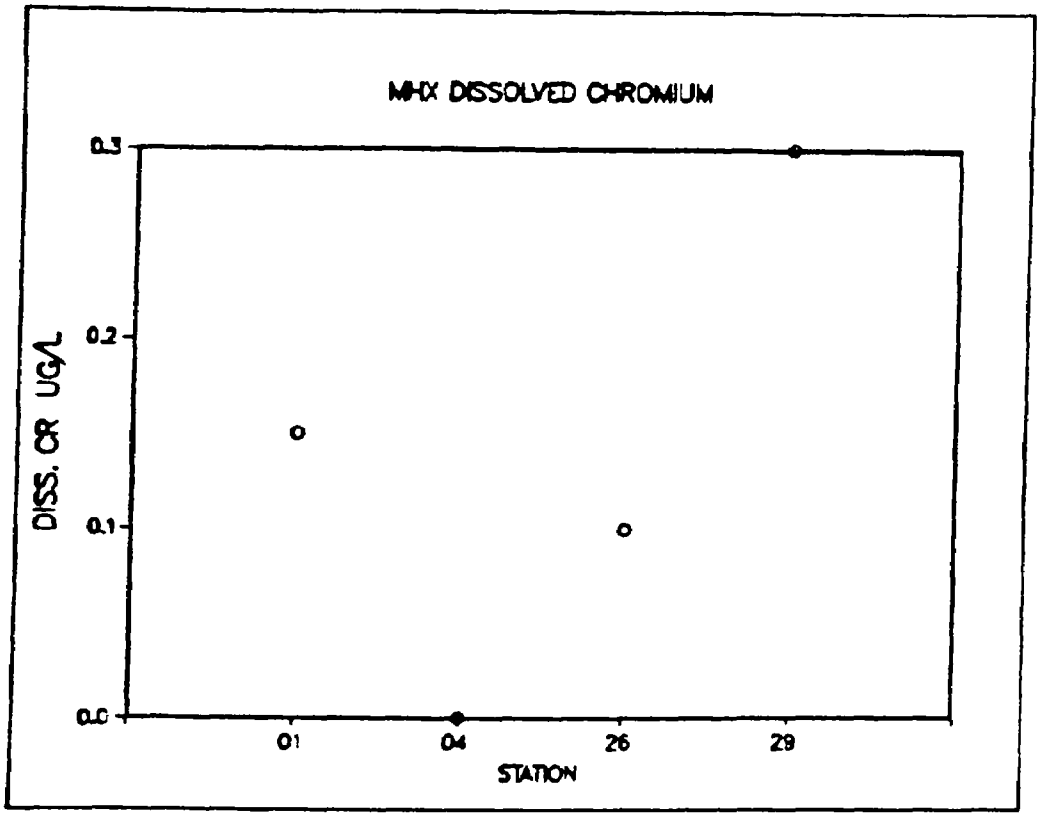
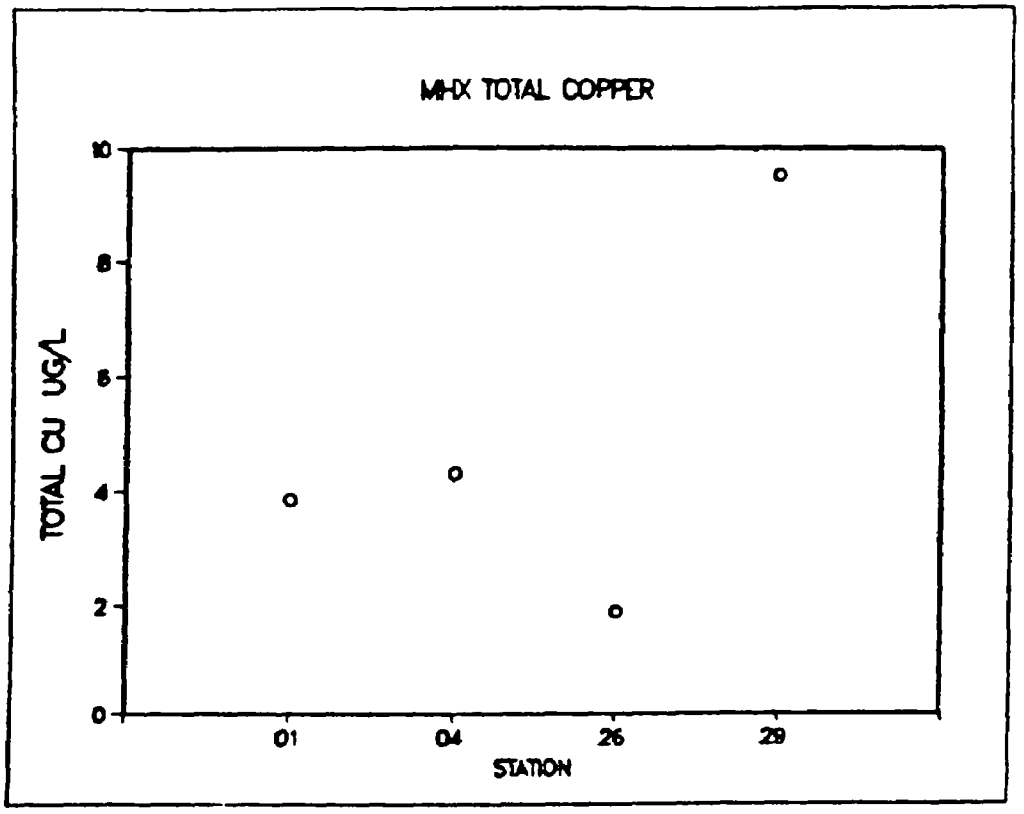


Figure 4.39. Spatial profile of total and dissolved chromium in grab and composite water samples. Monroe Harbor, Survey 10. (See map, Figure 2.6).



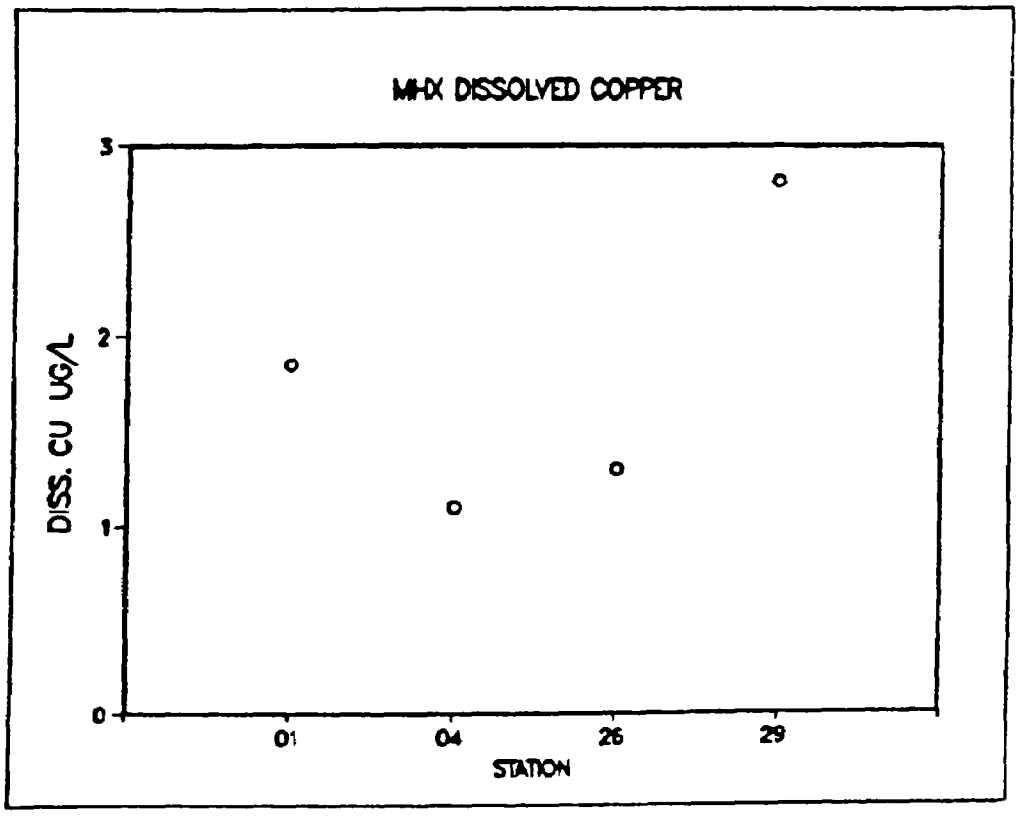
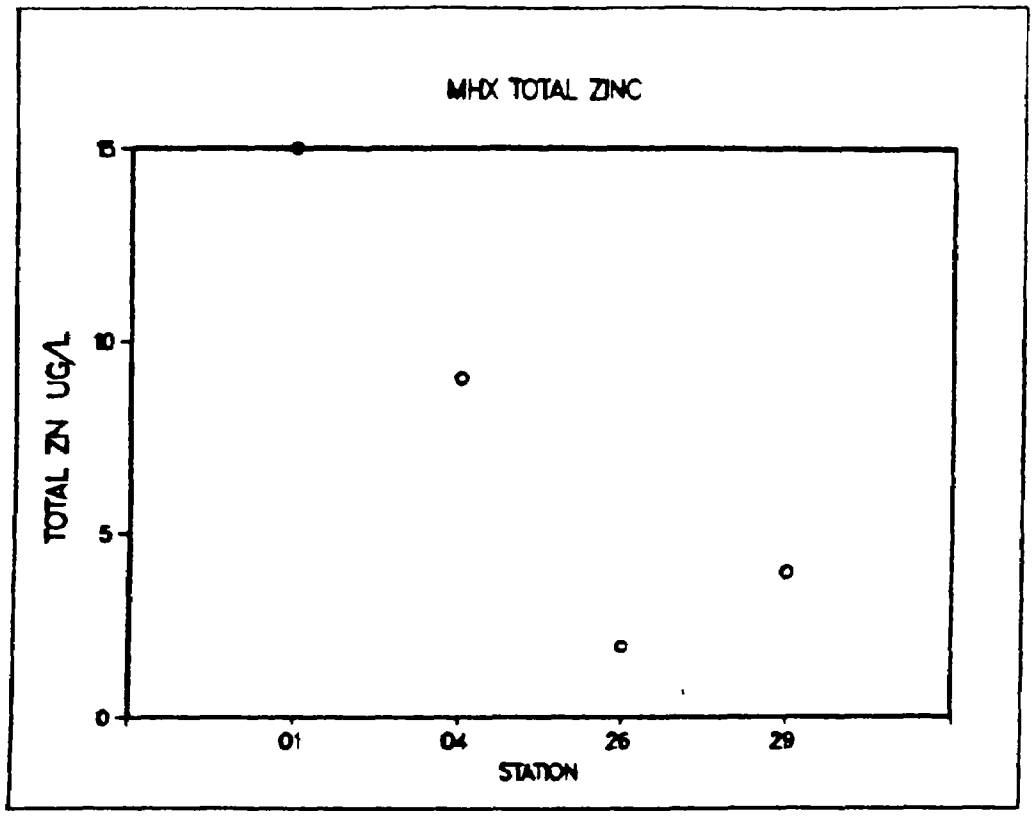


Figure 4.40. Spatial profile of total and dissolved copper in grab and composite water samples. Monroe Harbor, Survey 10. (See map, Figure 2.6).



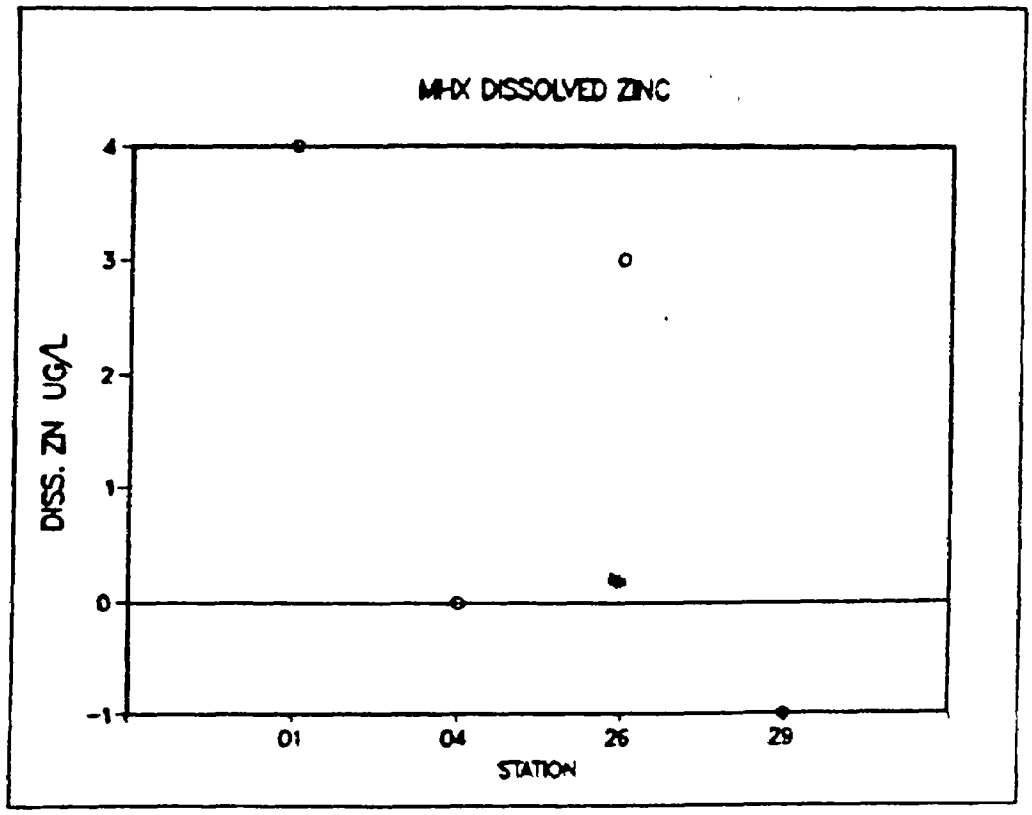
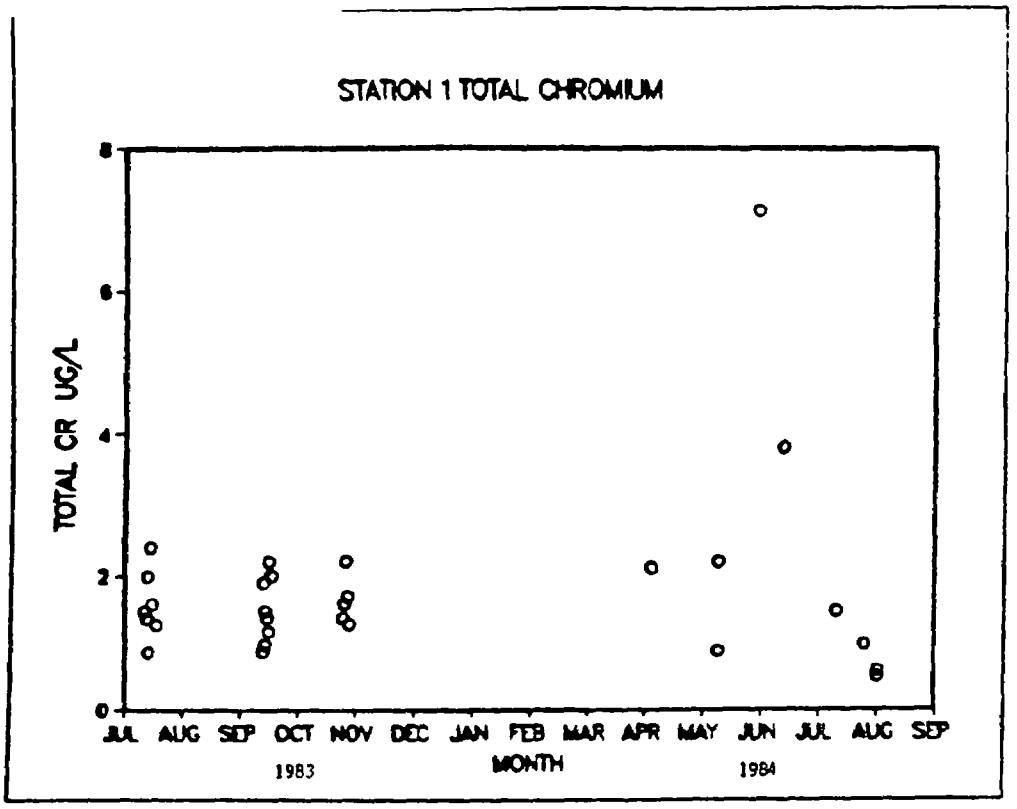


Figure 4.41. Spatial profile of total and dissolved zinc in grab and composite water samples. Monroe Harbor, Survey 10. (See map, Figure 2.6).



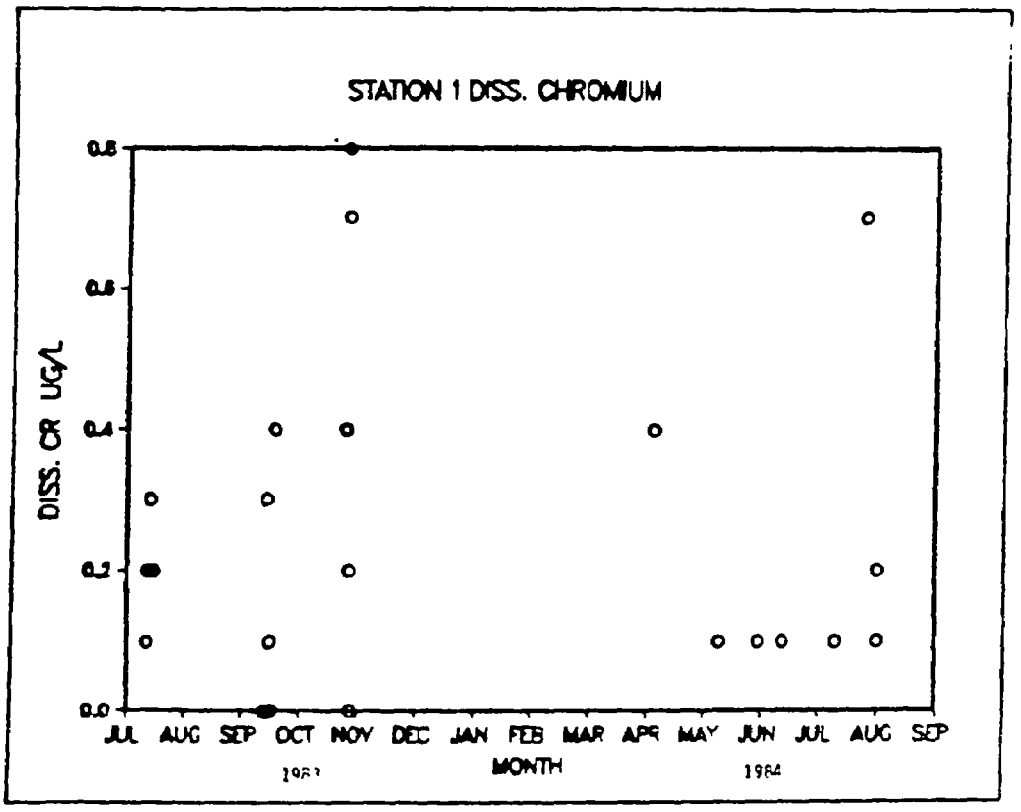
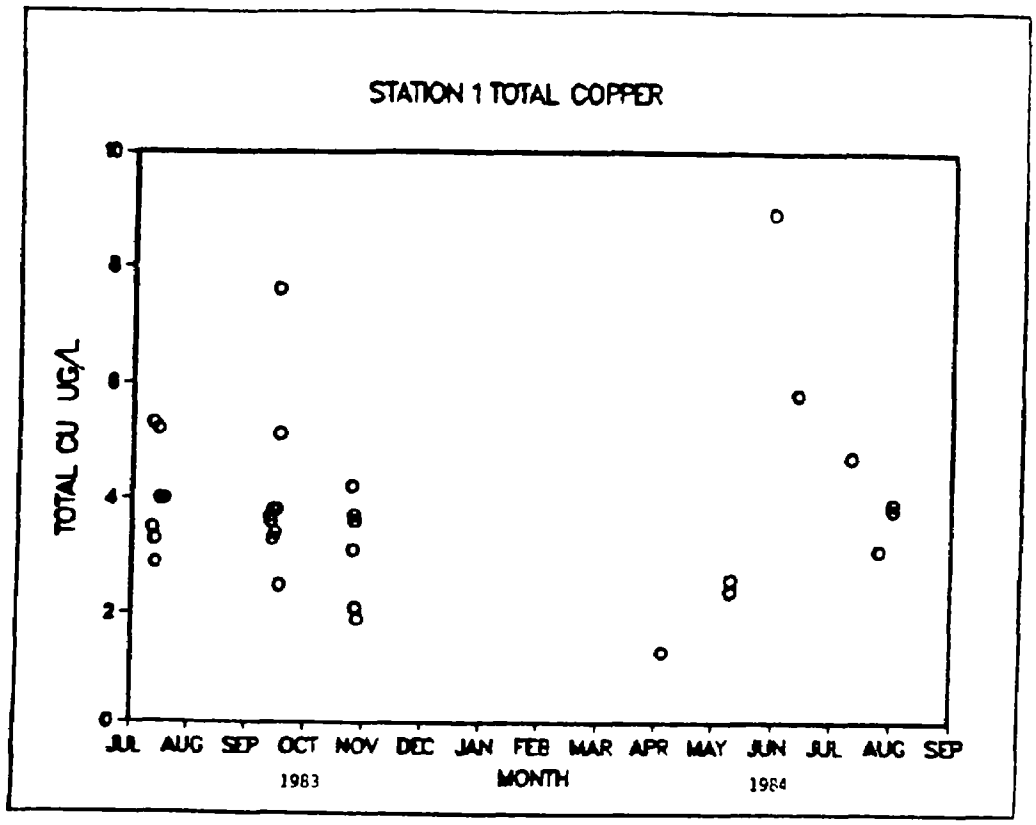


Figure 4.42. Temporal profiles of total and dissolved chromium at Station 1; Monroe Harbor, Surveys 1-10.



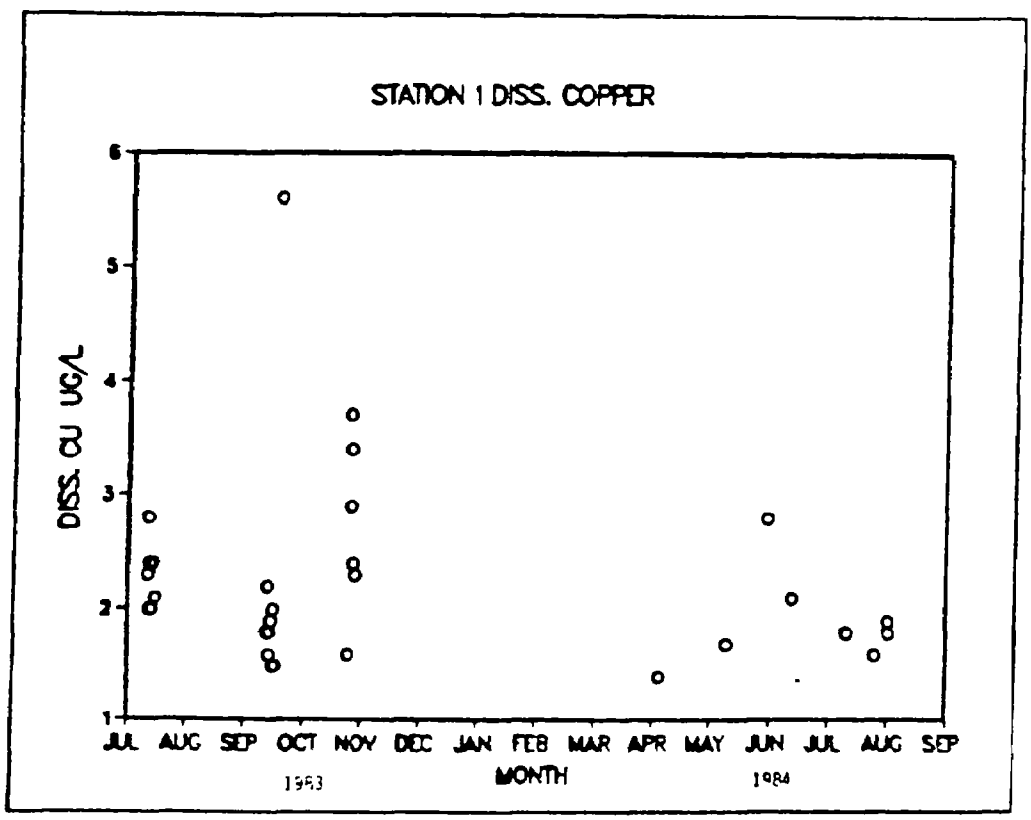
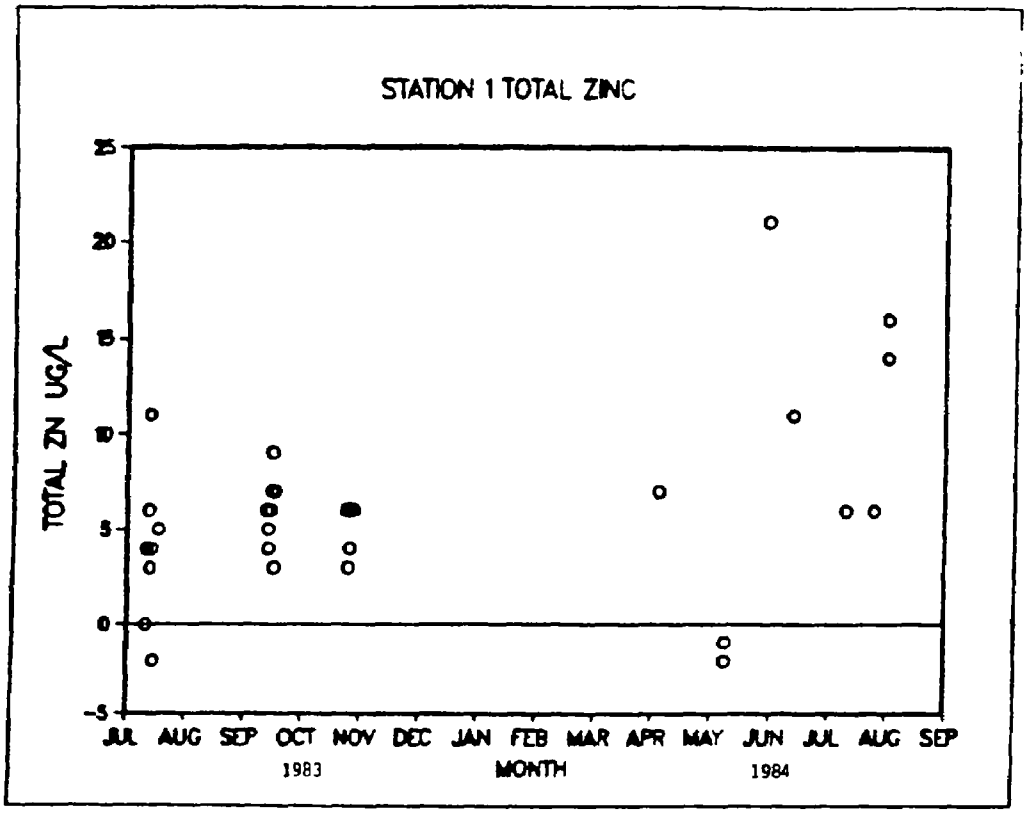


Figure 4.43. Temporal profiles of total and dissolved copper at Station 1; Monroe Harbor, Surveys 1-10.



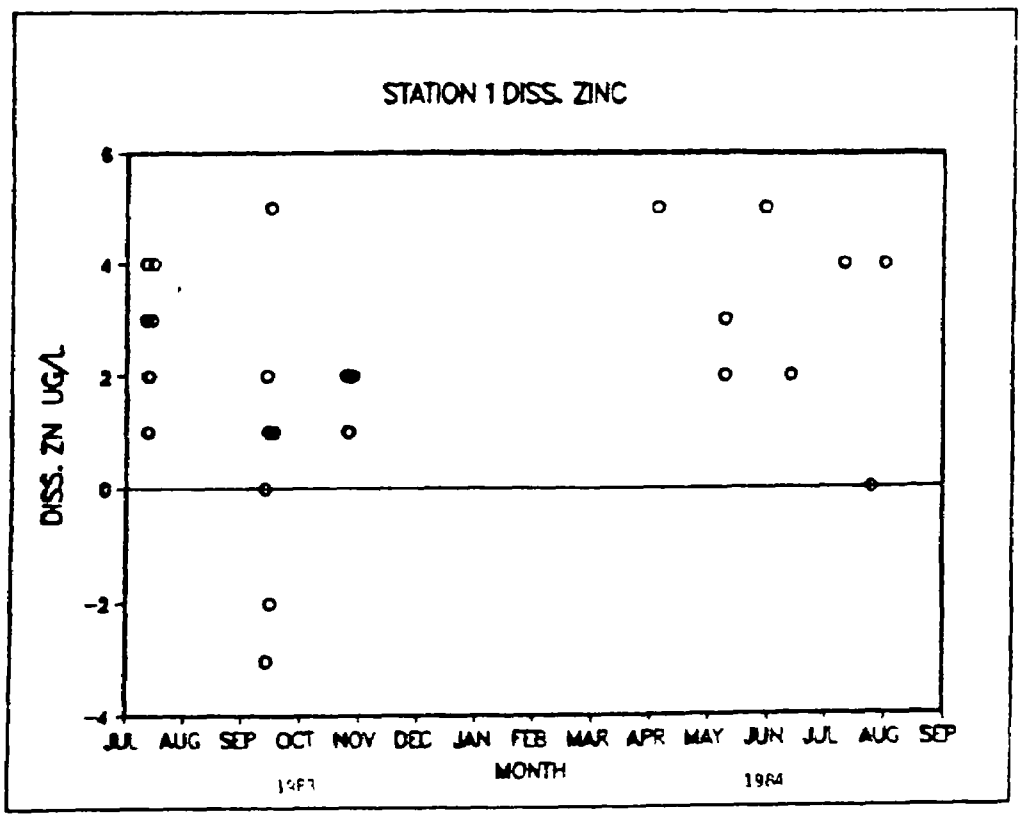
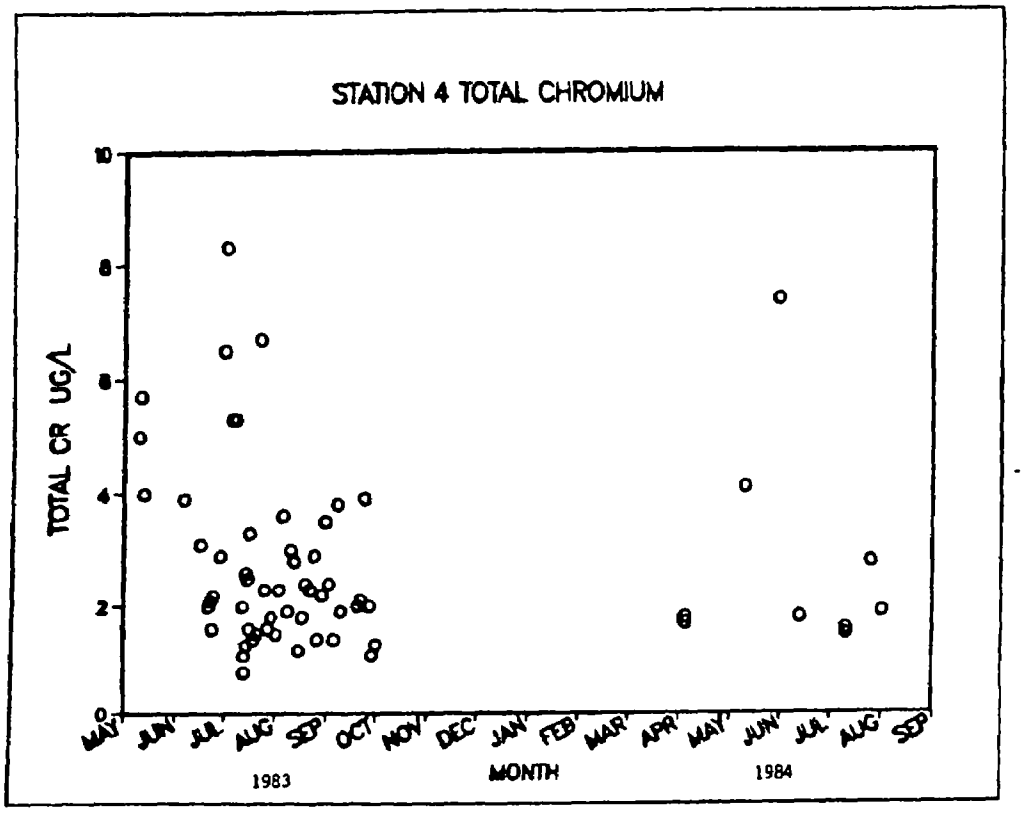


Figure 4.44. Temporal profiles of total and dissolved zinc at Station 1; Monroe Harbor, Surveys 1-10.



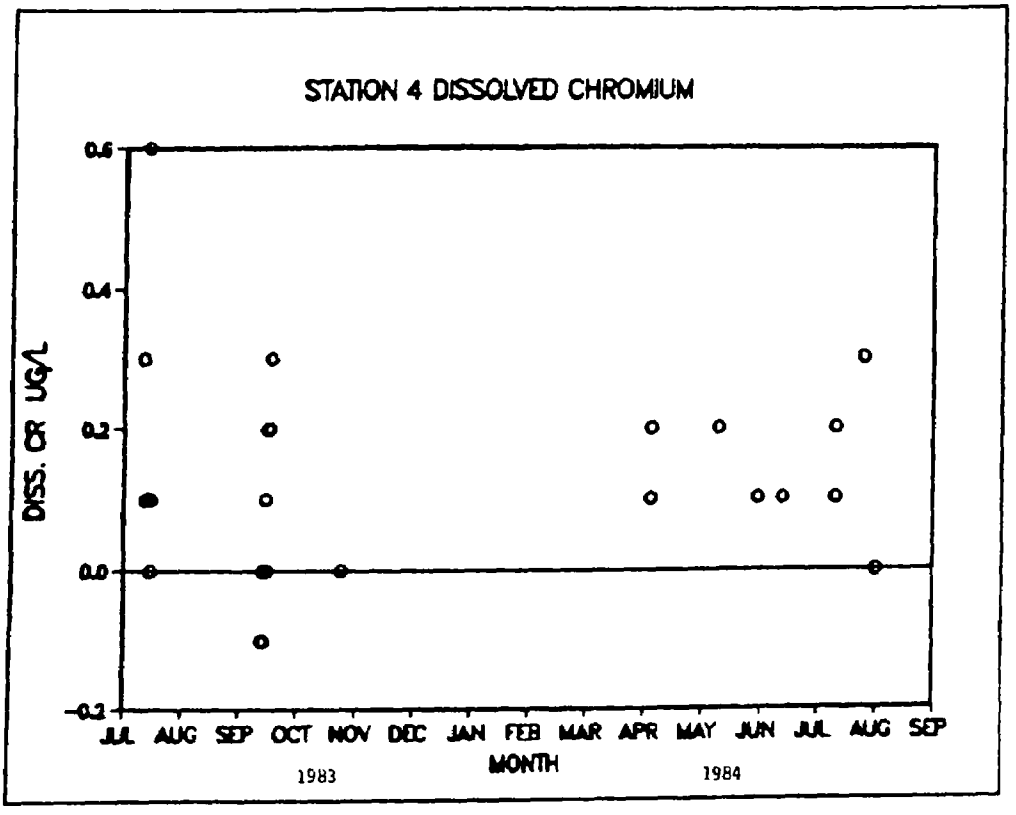
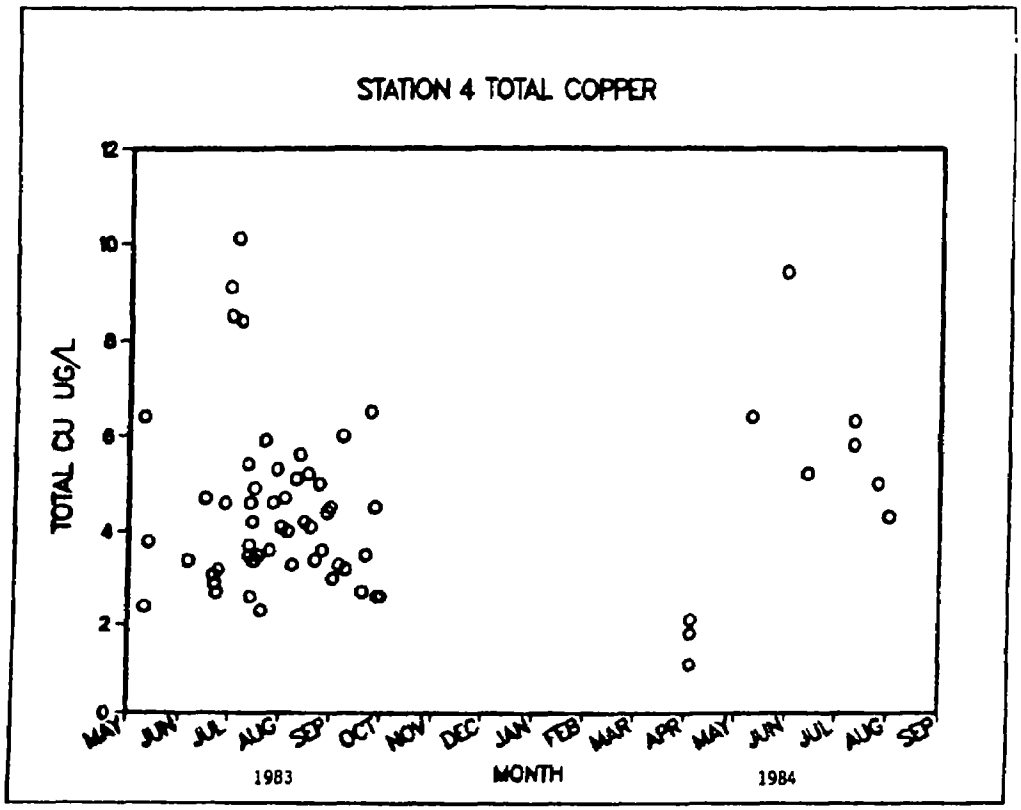


Figure 4.45. Temporal profiles of total and dissolved chromium at Station 4; Monroe Harbor, Surveys 1-10.



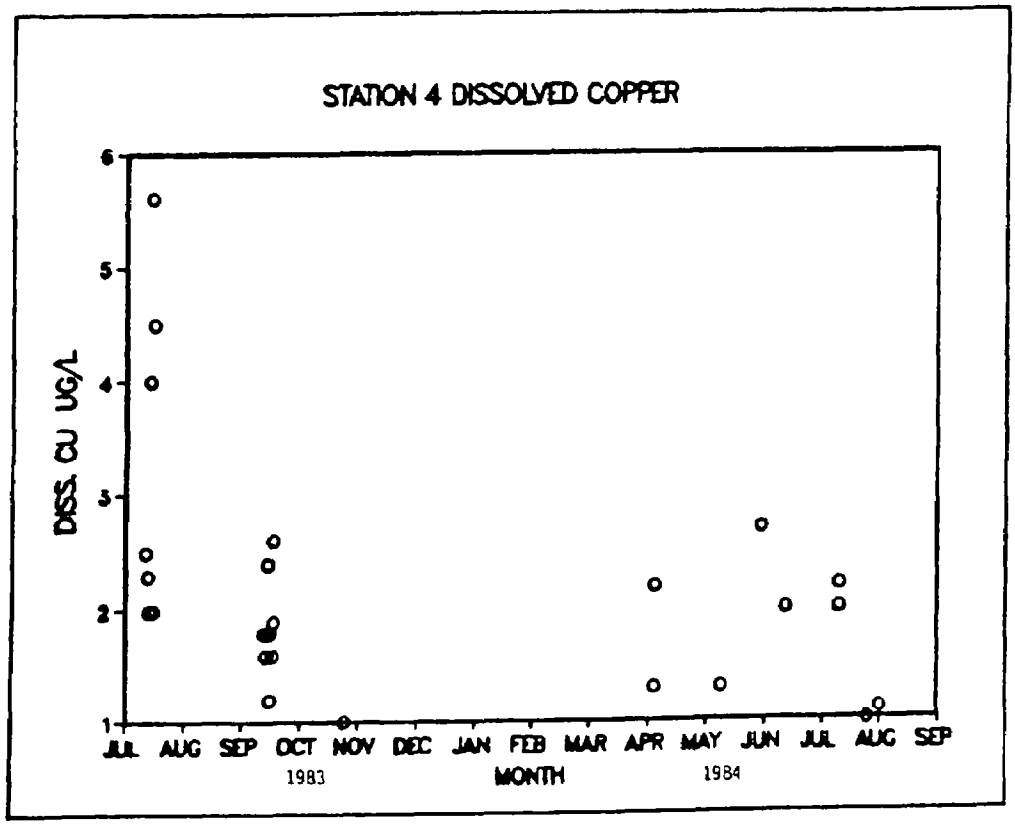
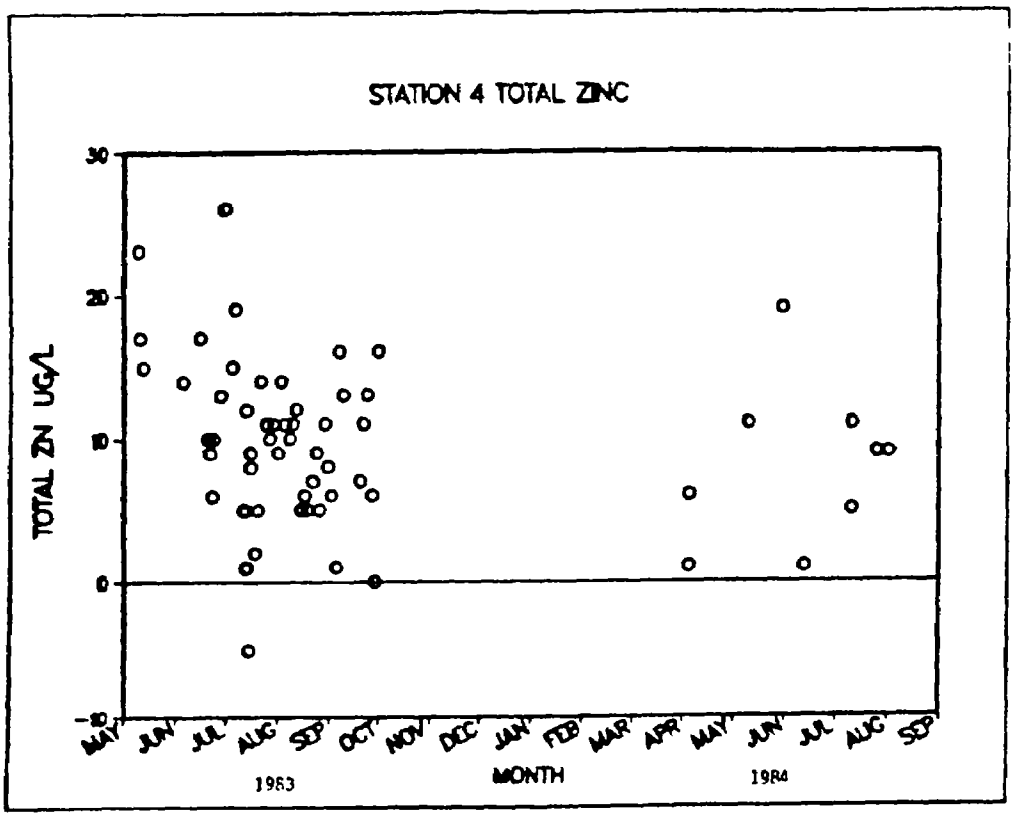


Figure 4.46. Temporal profiles of total and dissolved copper at Station 4; Monroe Harbor, Surveys 1-10.



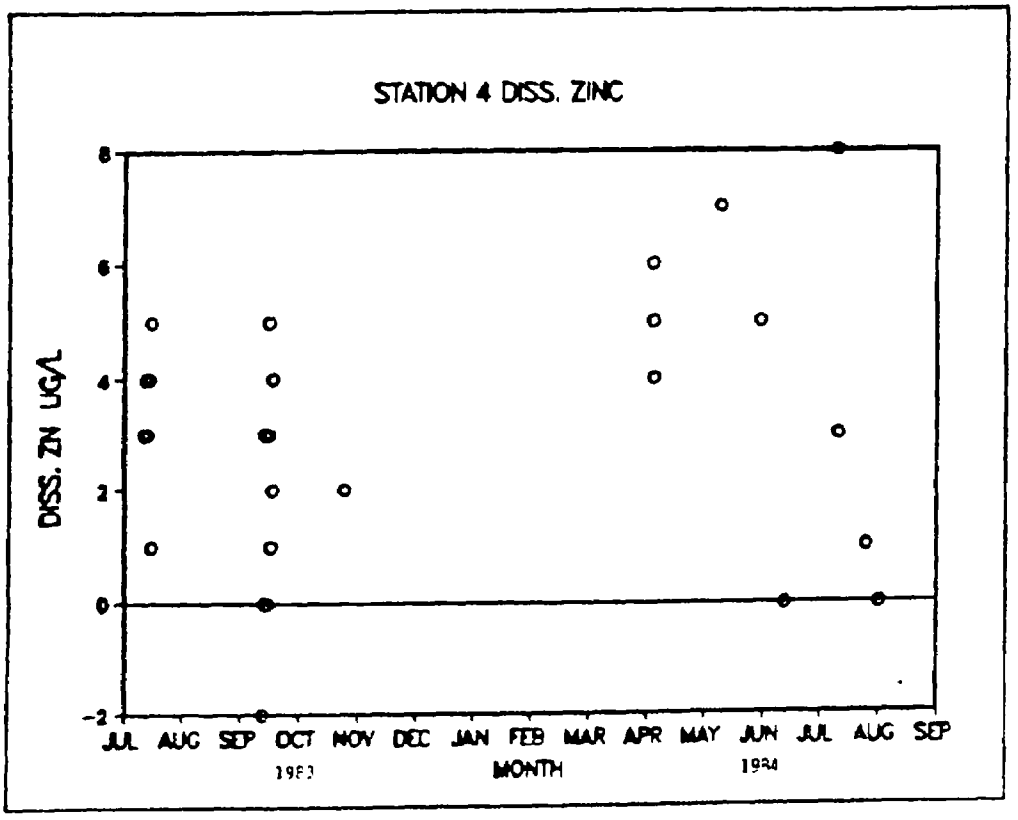


Figure 4.47. Temporal profiles of total and dissolved zinc at Station 4; Monroe Harbor, Surveys 1-10.

TABLE 3.1. SURVEY SAMPLING STRATEGY

Survey	Date	Stations Sampled	Sample Types Collected		Comments
			Grab	Composite	
I	July 12-17, 1983	Fig. 3.1	TO, TM, DM	TO, DO, TM, DM	No DO on Stations 7, 8, 9 or 10
II	September 13-18	Fig. 3.2	TO, TM, DM	TO, DO, TM, DM	
III	Oct. 25 - Nov. 1	Fig. 3.3	TO, DO, TM, DM	TO, DO, TM, DM	DO only on Stations 11, 14, 17, & 19
IV	April 2-5, 1984	Fig. 3.4	TO, PO, TM, DM	Not Collected	
V	May 9	Fig. 3.5	TO, PO, TM, DM	Not Collected	TO and PO only from Stations 1 & 4
VI	May 30	Fig. 3.6	TO, PO, TM, DM	Not Collected	TO and PO only from Stations 1 & 4
VII	June 12	Fig. 3.6	TO, PO, TM, DM	Not Collected	TO and PO only from Stations 1 & 4
VIII	July 10	Fig. 3.6	TO, PO, TM, DM	Not Collected	TO and PO only from Stations 1 & 4
IX	July 25	Fig. 3.6	TO, PO, TM, DM	Not Collected	TO and PO only from Stations 1 & 4
X	August 1	Fig. 3.6	TO, PO, TM, DM	Not Collected	TO and PO only from Stations 1 & 4

TO = Total organics
DO = Dissolved organics
PO = Particulate organics
TM = Total metals
DM = Dissolved metals

TABLE 3.2. STATION DESCRIPTIONS

Station No.	Description
1	Farthest upstream; by Winchester Road Bridge
2	Off of commercial marina
3	Off of WWTP outfall
4	At downstream edge of turning basin
5	Off of Ford Motor Company outfall
6	Just off of river mouth
7	WWTP; post-chlorination well
8	Tributary; Mason Run
9	Ford Motor Company outfall; just after settling lagoon
10	Ford Motor Company intake, of Lake Erie water
11	Lake Erie
12	Control site for biological projects; not reported here
13	WWTP plume station; Survey III only
14	WWTP plume station; Survey III only
15	WWTP plume station; Survey III only
16	WWTP plume station; Survey III only
17	WWTP plume station; Survey III only
18	WWTP plume station; Survey III only
19	WWTP plume station; Survey III only
20	Upstream of tributary; Mason Run; Survey IV only
21	Between WWTP and turning basin; Survey IV only
22	Between turning basin and Detroit Edison intake, Survey IV only
23	Between turning basin and Detroit Edison intake, Survey IV only
24	Detroit Edison intake; Survey IV only
25	Monroe City drinking water intake
26	River mouth
28	Between Detroit Edison intake and river mouth
29	Detroit Edison discharge canal
30	Nearshore Lake Erie; Survey IV only
31	Nearshore Lake Erie; Survey IV only
32	Nearshore Lake Erie; Survey IV only
33	Nearshore Lake Erie; Survey IV only
34	Nearshore Lake Erie; Survey IV only
35	Nearshore Lake Erie; Survey IV only
36	Nearshore Lake Erie; Survey IV only
37	Nearshore Lake Erie; Survey IV only
38	Nearshore Lake Erie; Survey IV only
39	Toxicity test control water; Port Huron pump station
40	Toxicity test control water; Reconstituted water
41	Nearshore Lake Erie; Survey V only
42	Nearshore Lake Erie; Survey V only
43	Nearshore Lake Erie; Survey V only
44	Nearshore Lake Erie; Survey V only
45	Nearshore Lake Erie; Survey V only
46	Nearshore Lake Erie; Survey V only
47	Nearshore Lake Erie; Survey V only

TABLE 3.3. DETECTION LIMITS - METALS

Metal	Detection Limit (μg/L)	Analytical Method
Chromium	.25	Perkin-Elmer 460 Flameless Atomic Absorption using 50 μL
Copper	.31	Perkin-Elmer 460 Flameless Atomic Absorption using 50 μL
Zinc	4	Perkin-Elmer 603 Flame Atomic Absorption

TABLE 3.4. MONROE HARBOR STUDIES SAMPLE BLANKS - METALS

(Note: B.B. = Batch Blank and F.B. = Filter Blank)

Metal	Monroe Harbor Survey #	No. Samples (B.B., F.B.)	Mean µg/L (B.B., F.B.)	Standard Deviation µg/L (B.B., F.B.)	T-Test Result
Copper	1	[12, 12]	[W.16, .72]	[T.31, 1.02]	*Same
Copper	2	[18, 17]	[T.31, T.31]	[.44, .51]	Same
Copper	3	[8, 8]	[W.16, T.31]	[W.16, W.16]	Same
Copper	[4,5,6]	[9, 9]	[W.16, T.31]	[.59, .60]	Same
Copper	[9, X]	[3, 3]	[T.31, T.31]	[.45, .36]	Same
Copper	[Z]	[-, 4]	[-, W.16]	[-, W.16]	Same
Chromium	1	[11, 12]	[W.12, W.12]	[W.12, W.12]	Same
Chromium	2	[18, 18]	[W.12, W.12]	[T.25, W.12]	Same
Chromium	3	[8, 8]	[W.12, W.12]	[W.12, W.12]	Same
Chromium	[4,5,6]	[9, 9]	[W.12, W.12]	[W.12, W.12]	Same
Chromium	[9, X]	[3, 3]	[W.12, W.12]	[W.12, W.12]	Same
Chromium	[Z]	[-, 4]	[-, W.12]	[-, W.12]	Same
Zinc	1	[12, 12]	[W2, W2]	[W2, W2]	Same
Zinc	3	[18, 18]	[W2, W2]	[W2, W2]	Same
Zinc	5	[8, 8]	[W2, W2]	[T4, W2]	Same
Zinc	[4,5,6]	[9, 9]	[W2, W2]	[T4, T4]	Same
Zinc	[9, X]	[3, 3]	[W2, W2]	[W2, W2]	Same
Zinc	[Z]	[-, 4]	[-, W2]	[-, W2]	Same

*At the 95% confidence level, the mean batch blanks and filter blanks were equal; therefore, no blank correction was needed for the filtering process.

Results less than the detection limit but greater than or equal to half the detection limit are preceded by "T". The detection limit follows the "T".

Results less than half the detection limit are preceded by a "W". One-half the detection limit follows the "W".

TABLE 3.5. INTERCOMPARISON WITH USEPA ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY, CINCINNATI

(Concentrations in μg/L)

Metal:Series	LLRS Result	Measured Mean Recovery Reported by EPA $\bar{X}$	QC True Value (Designed)	Mean Recovery ± 2 Standard Deviations (95% Confidence Level)
Copper: WP475 (#4)	11	11.3	11	6.1 - 16.5
Copper: WP475 (#6)	328	346	350	311 - 381
Chromium: WP475 (#6)	234	242	250	196 - 288
Chromium: WP475 (#4)	10	10.2	10	8.0 - 12.4
Chromium: WS378 (#2)	19	18.2	18	(15.1 - 21.3)
Chromium: WS378 (#13)	50	46.0	46	(38.9 - 53.1)
Zinc: WP475 (#4)	13	17.1	16	9.7 - 24.5
Zinc: WP475 (#6)	393	396	400	352 - 440

TABLE 3.6. PERCENT RECOVERIES CALCULATED FROM STANDARD ADDITIONS ON SAMPLES FROM THE MONROE HARBOR STUDY

Metal	Number of Samples	Mean Percent Recovery	Standard Deviation
Dissolved Copper	87	101	28
Total Copper	127	108	27
Dissolved Zinc	89	104	22
Total Zinc	139	104	14
Dissolved Chromium	357	139	20
Total Chromium	419	126	19

TABLE 3.7. RESULTS OF FIELD DUPLICATES, MONROE HARBOR STUDY, 1983-1984

Metal	River Samples		Lake Samples		WWTP Samples (Station 7)	
	Number of Pairs	Standard Deviation (μg/L)	Number of Pairs	Standard Deviation (μg/L)	Number of Pairs	Standard Deviation (μg/L)
Dissolved Zinc	16	3	-	-	4	1
Total Zinc	15	3	4	3	-	-
Dissolved Chromium	12	.05	5	.13	5	.60
Total Chromium	15	.34	4	.20	4	.14
Dissolved Copper	9	.36	4	.26	-	-
Total Copper	11	.47	-	-	-	-

Detection Limits (μg/L), Zinc = 4, Chromium = .25, Copper = .31

TABLE 3.8. VARIATION OF DUPLICATES FROM LAKE ERIE DURING STORM CONDITIONS (SURVEY IV)

Metal	Station 35	Station 38
	$*\lvert C_1 - C_1 \rvert$ (μg/L)	$*\lvert C_2 - C_2 \rvert$ (μg/L)
Dissolved Zinc	8	1
Total Zinc	3	15
Dissolved Chromium	.03	.08
Total Chromium	3.6	1.5
Dissolved Copper	1.1	2.1
Total Copper	-	-

*C_1 is the first measurement
C_2 is the second measurement

TABLE 3.9. MONROE HARBOR BETWEEN RUN SAMPLE REPLICATES

Sample Name*	Source	Chromium (μg/L)	Copper (μg/L)	Zinc (μg/L)
		Number, Mean, Standard Deviation	Number, Mean, Standard Deviation	Number, Mean, Standard Deviation
MHQCT001	River Raisin Water (Total)	6, 2.0, .32	7, 3.8, .96	7, 5, 4
MHQCT002	Monroe WWTP (Total)	4, 2.2, .58	4, 9.6, 1.60	4, 41, 2
MHQCT003	Nearshore Lake Erie (Total)	7, 2.3, .58	6, 4.4, .79	6, 10, 6
MHQCD001	River Raisin Water (Dissolved)	3, .27, .09	-	4, 2, 4
MHQCD002	Monroe WWTP (Dissolved)	3, .19, .10	-	-

*These samples were composites of samples and were prepared in the laboratory for Q.C. purposes only.

TABLE 3.10. EXTRACTION EFFICIENCY OF PARTICULATE FILTERS

SAMPLE I.D.	1ST EXTRACTION (ng/L)	2ND EXTRACTION (ng/L)	% EFFICIENCY
MH4006PTS4N1	9.8	1.3	88
MH4006PTS4N2	11	0.15	99
MH4007PTB4N1	14	0.20	99
MH4009PT26N1	17	0.34	98

TABLE 3.11. DUPLICATE SAMPLE ANALYSIS

SURVEY	SAMPLE I.D.	TOTAL PCB (ng/L)		STANDARD DEVIATION (ng/L)	COEFFICIENT OF VARIATION
		MEAN	RANGE		
1	MH1002WT01C1	12	11-13	1.4	0.12
	MH1013WT04C1	34.5	32-37	3.9	0.11
	MH1519WT08C1	310	300-320	0.98	0.0034
2	MH2002WT01C1	11	10-12	1.2	0.11
	MH2016WTS4C1	255	250-260	10	0.04
	MH2017WTB4C1	325	310-340	22	0.068
	MH2031WT06C1	32	24-40	11	0.35
	MH2087WTS4N1	545	460-630	120	0.21
	MH2088WTB4N1	300	270-330	47	0.16
3	MH3002WT03C1	15.5	9-22	9.1	0.59
	MH3002WF03C1	13.5	11-16	3.7	0.28
	MH3009WT03N1	4.35	4.2-4.5	0.19	0.043
	MH3020WF01N1	3.35	3.1-3.6	0.36	0.11
	MH3042WT15N1	4.0	3.8-4.2	0.27	0.068
4	MH4006WTS4N1	16	13-19	4.2	0.27
	MH4006PTS4N1	10.4	9.8-11	0.7	0.068
8	MH8002WT04N1	85	50-120	48	0.57
	MH8002PT04N1	70.5	63-78	79	0.16
10	MHX001WT01N1	4.45	4.3-4.6	0.19	0.042

TABLE 3.12. REPLICATE ANALYSIS OF PCB QC STANDARDS

Number	True Concentration (ng/mL)	Mean (ng/mL)	Range (ng/mL)	Standard Deviation (ng/mL)	Coefficient of Variation
5	107.6	110	100-120	8.2	0.076
22	245	240	160-300	31	0.13
3	258.3	240	220-260	23	0.093
58	270	250	190-300	27	0.11

TABLE 3.13. REPLICATE ANALYSIS OF AROCLOR MIXTURES

Aroclor Mixture	Number	True Concentration (ng/mL)	Mean (ng/mL)	Range (ng/mL)	Standard Deviation (ng/mL)	Coefficient of Variation
1221	12	129.6	130	86-160	26	0.20
1016	6	26.2	29	27-31	1.6	0.055
1016	3	63.0	78	76-81	3	0.038
1254	8	16.2	15	14-17	1.3	0.086
1254	11	43.2	45	39-58	6.3	0.14
1262	10	36.8	54	42-78	11	0.20

TABLE 4.1. TOTAL PCB IN COMPOSITE AND GRAB WHOLE WATER SAMPLES, MONROE HARBOR, SURVEY 1

DATE		SAMPLE TYPE	SAMPLE NUMBERS										
			1	2	7	3	8	4	9	10	5	6	11
JULY 12	Total PCB ng/L	C	11/13	5.2		6.6	86	35		54		6.0	
		G											7.8
	% System Blank	C	(-)/(-)	(-)		(-)	(-)	(-)		(-)		(-)	
		G											(-)
JULY 13	Total PCB ng/L	C	8.3	7.4	34	5.1	80	32/37		67		14	
		G	3.7	3.3	37	8.7	140	27		44		8.5	
	% System Blank	C	(-)	(4)	(3)	(3)	(0)	(1)/(1)		(1)		(1)	
		G	(2)	(-)	(0)	(-)	(1)	(1)		(-)		(3)	
JULY 14	Total PCB ng/L	C	12	11		13	96	20		66		26	
		G											7.8
	% System Blank	C	(2)	(3)		(9)	(38)	(3)		(32)		(6)	
		G											(1)
JULY 15	Total PCB ng/L	C	12			12	79	21		71		19	
		G	6.8	7.4		8.7	75	24		50		13	9.7
	% System Blank	C	(21)			(47)	(-)	(7)		(-)		(3)	
		G	(1)	(3)		(1)	(1)	(1)		(1)		(0)	(1)
JULY 16	Total PCB ng/L	C	7.3	7.7		8.6	320/300	210		50		9.2	
		G											8.7
	% System Blank	C	(4)	(1)		(0)	(-)/(-)	(0)		(0)		(2)	
		G											(0)
TOTAL PCB (C&G) MEAN ± S.D. (RANGE)			9.3+3.2 (3.7-13)	7.0+2.6 (3.3-11)	34	8.9+2.8 (5.1-13)	147+103 (75-320)	51+65 (20-210)		57+10 (44-71)		14+6.9 (6-26)	9.7

C = Composite Sample
G = Grab Sample

TABLE 4.2. TOTAL PCB IN COMPOSITE FILTRATE WATER SAMPLES, MONROE HARBOR, SURVEY 1

DATE		STATION NUMBERS										
		1	2	7	3	8	4	9	10	5	6	11
JULY 12	Total PCB ng/L	23	22		19		20		16	16	11	
	% System Blank	(5)	(5)		(6)		(3)		(1)	(2)	(5)	
JULY 13	Total PCB ng/L	6.3	11									
	% System Blank	(-)	(4)									

TABLE 4.3. TOTAL PCB IN COMPOSITE AND GRAB WHOLE WATER SAMPLES, MONROE HARBOR, SURVEY 2

DATE		SAMPLE TYPE	STATION NUMBERS										
			1	7	3	8	S4	B4	9	10	5	6	11
SEPT 13	Total PCB ng/L	C	10/12		100	340	450	280		160		30	
		G				730		470		67		40	28
	% System Blank	C	(7)/(5)		(3)	(2)	(1)	(1)		(1)		(9)	
		G				(1)		(1)		(1)		(2)	(12)
SEPT 14	Total PCB ng/L	C	12		170	290	510	170		70		17	
		G			240								20
	% System Blank	C	(26)		(8)	(1)	(5)	(4)		(3)		(17)	
		G			(1)								(3)
SEPT 15	Total PCB ng/L	C	10		130	210	250/260	340/310		62		41	
		G	9.9			460	210	170		110		44	24
	% System Blank	C	(30)		(6)	(0)	(6)/(4)	(3)/(3)		(0)		(12)	
		G	(4)			(0)	(0)	(1)		(3)		(1)	(3)
SEPT 16	Total PCB ng/L	C	8.2		60	410	130	350		57		21	
		G			18								44
	% System Blank	C	(8)		(3)	(0)	(2)	(1)		(0)		(3)	
		G			(2)								(2)
SEPT 17	Total PCB ng/L	C	5.0		68		590	240		55		24/40	
		G	13				460/630	270/330		74			42
	% System Blank	C	(12)		(0)		(0)	(0)		(2)		(1)/(0)	
		G	(15)				(1)/(0)	(0)/(0)		(4)			(5)
TOTAL PCB (C&G) MEAN ± S.D. (RANGE)			10±2.5 (5-12)		112±75 (60-240)	407±181 (210-730)	388±179 (130-630)	293±90 (170-470)		82±36		32±10 (17-44)	32±11 (20-44)

C = Composite Sample
G = Grab Sample

TABLE 4.4. TOTAL PCB IN COMPOSITE WHOLE (A) AND FILTRATE (B), MONROE HARBOR, OCTOBER 25, SURVEY 3

(A)

	STATION NUMBERS							
	1	3	8	4S	4B	10	6	11
Total PCB ng/L	11	22/9	-	220	140	-	17	220
% System Blank	(140)	(85/118)	-	(17)	(18)	-	(77)	(20)

(B)

	STATION NUMBERS							
	1	3	8	4S	4B	10	6	11
Total PCB ng/L	6.3	16/11	56	110	73	21	6.3	9.2
% System Blank	(0)	(0)/(0)	(7)	(0)	(0)	(9)	(6)	(22)
Filtrate/Whole PCB	0.57	0.73/1.22	-	0.52	0.52	-	0.37	0.44

TABLE 4.5. TOTAL PCB IN GRAB WHOLE WATER SAMPLES, MONROE HARBOR, WWTP PLUME, SURVEY 3

DATE		STATION NUMBERS						
		13	14	15	16	17	18	19
OCT 26	Total PCB ng/L	-	6	6	5.6	4.7	6.2	17
	% System Blank	-	(11)	(8)	(5)	(9)	(3)	(1)
OCT 27	Total PCB ng/L	-	46	4	7.7	8.3	8.4	7.8
	% System Blank	-	-	-	-	-	-	-
OCT 28	Total PCB ng/L	23	2.1	3.8/4.2	3.7	8.5	4.2	48
	% System Blank	(1)	(0)	(6)/(11)	(4)	(1)	(1)	(5)
	Total PCB	23	18±24 (2.1-46)	4.5±1.0 (3.8-4)	5.7±2.0 (3.7-7.7)	7.2±2.1 (4.7-8.5)	6.3±2.1 (4.2-8.4)	24.3±21 (7.8-48)

TABLE 4.6. TOTAL PCB IN GRAB FILTRATE WATER SAMPLES, MONROE HARBOR, WWTP PLUME, SURVEY 3

DATE		STATION NUMBERS						
		13	14	15	16	17	18	19
OCT 26	Total PCB ng/L	-	6.2	-	-	2.2	-	3.6
	% System Blank	-	(6)	-	-	(5)	-	(4)
OCT 27	Total PCB ng/L	-	4.4	-	-	14	-	10
	% System Blank	-	(6)	-	-	(10)	-	(4)
OCT 28	Total PCB ng/L	-	6.6	-	-	2.7	-	9.3
	% System Blank	-	(1)	-	-	(5)	-	(4)
	Total PCB	-	5.7±1.2 (4.4-6.6)	-	-	6.3±6.7 (2.2-14)	-	7.6±3.5 (3.6-10)

TABLE 4.7. TOTAL PCB IN GRAB WHOLE WATER (A) AND PARTICULATE (B) SAMPLES, MONROE HARBOR, SURVEY 4

(A)

	STATION NUMBERS														
	1	7	21	20	8	4S	4B	22	22S	23B	24	28	26	11	29
Total PCB ng/L (April 4, 1984)	12	8.9	12	14	19	19/13	26	21	25	31	17	-	8	18	19
% System Blank	-	(11)	(5)	(8)	(1)	(3)/-	(2)	(0)	(3)	(2)	-	-	(3) (3)*	(4)	(1)

*% Florisil blank.

(B)

	STATION NUMBERS														
	1	7	21	20	8	4S	4B	22	22S	23B	24	28	26	11	29
Total PCB ng/L (April 4, 1984)	4.1	4.1	5.3	36	13	9.8/11	14	26	17	28	22	17	17	11	29
% System Blank	(6)	(6)	-	(2)	(4)	(2)/(3)	(2)	-	-	-	-	-	(1)	-	-
% Florisil Blank	(9)	(6)	(11)	(3)	(6)	-/-	-	(6)	(6)	(6)	(5)	(5)	(4)	(7)	(5)
Particulate/-Whole PCB	0.34	0.46	0.44	2.57	0.68	0.52/-0.85	0.54	0.51	0.68	0.90	1.29	-	2.1	0.61	1.53

TABLE 4.8. TOTAL PCB IN GRAB WHOLE WATER (A) AND PARTICULATE (B) SAMPLES AT STATION 1, MONROE HARBOR, SURVEYS 5-10

STATION 1		SURVEY					
		5	6	7	8	9	10
A	Total PCB ng/L	5.9	13	8.4	6.9	4.9	4.6/4.3
	% System Blank	(3)	(6)	(6)	(6)	(13)	(28)/(10)
B	Total PCB ng/L	1.8	8.4	2.7	2.4	-	-
	% System Blank	(29)	(14)	(20)	(3)	-	-

TABLE 4.9. TOTAL PCB IN GRAB WHOLE WATER (A) AND PARTICULATE (B) SAMPLES AT STATION 4, MONROE HARBOR, SURVEYS 5-10

STATION 4		SURVEY					
		5	6	7	8	9	10
A	Total PCB ng/L	110	14	6.7	120/50	93	210
	% System Blank	(1)	(3)	(8)	(3)/(5)	(3)	(1)
B	Total PCB ng/L	110	18	-	63/78	72	-
	% System Blank	(3)	(7)	-	(8)/(6)	-	-

TABLE 4.10. SPATIAL PROFILES OF D SOLVED AND TOTAL METALS (μg/L), SURVEY 1

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	2.26 ± 0.225 (2.00 – 2.55)	3.87 ± 0.783 (2.90 – 5.20)	0.221 ± 0.057 (0.15 – 0.30)	1.59 ± 0.488 (0.9 – 2.4)	2.36 ± 1.18 (1.0 – 4.0)	4.14 ± 3.98 (-2.0 – 11.0)
2	2.87 ± 1.44 (1.80 – 5.50)	3.56 + 0.614 (2.70 - 4.30)	0.200 ± 0.082 (0.1 – 0.3)	1.24 ± 0.35 (0.6 – 1.8)	2.71 ± 1.11 (1.0 – 4.0)	4.37 ± 6.50 (-3.0 – 13.0)
7	4.12 ± 0.564 (3.60 – 5.30)	7.46 ± 5.94 (2.10 – 21.20)	0.407 ± 0.084 (0.3 – 0.5)	2.36 ± 2.09 (0.7 – 6.8)	22.6 ± 7.74 (14.0 – 38.0)	43.4 ± 15.7 (27.0 – 75.5)
3	2.15 ± 0.176 (2.00 – 2.40)	3.83 ± 1.04 (2.70 – 5.60)	0.183 ± 0.117 (0.1 – 0.4)	1.63 ± 0.596 (0.8 – 2.3)	3.83 ± 2.14 (0.0 – 6.0)	3.86 ± 8.21 (-12.0 – 15.0)
8	3.28 ± 1.26 (2.10 – 5.55)	6.66 ± 2.46 (4.50 – 12.30)	0.264 ± 0.103 (0.1 – 0.4)	3.24 ± 0.78 (2.1 – 4.25)	1.21 ± 1.78 (-1.0 – 4.0)	8.63 ± 7.85 (-1.0 – 26.0)
4	3.27 ± 1.43 (2.00 – 5.60)	4.03 ± 0.918 (2.60 – 5.40)	0.186 ± 0.204 (0.0 – 0.6)	1.96 ± 0.793 (0.95 – 3.30)	3.29 ± 1.25 (1.0 – 5.0)	4.37 ± 5.34 (-5.0 – 12.0)
9	14.6 ± 5.28 (8.9 – 21.6)	42.0 ± 21.0 (18.5 – 72.2)	15.2 ± 9.97 (7.2 – 29.7)	32.0 ± 21.3 (10.0 – 60.2)	16.0 ± 5.16 (6.0 – 23.0)	80.3 ± 75.2 (31.0 – 251.0)
5	2.54 ± 1.24 (1.3 – 5.1)	5.36 ± 1.56 (3.6 – 8.6)	0.736 ± 0.673 (0.2 – 2.15)	2.76 ± 1.16 (1.5 – 4.45)	1.57 ± 1.27 (-1.0 – 3.0)	5.81 ± 5.69 (-2.5 – 15.0)
10	1.93 ± 0.55 (1.5 – 3.1)	6.33 ± 0.595 (5.5 – 7.1)	0.129 ± 0.076 (0.0 – 0.2)	3.89 ± 1.11 (2.7 – 6.4)	1.14 ± 2.41 (-1.0 – 5.0)	13.9 ± 7.53 (7.0 – 28.0)
6	1.83 ± 0.294 (1.5 – 2.3)	3.34 ± 0.866 (2.3 – 4.9)	0.25 ± 0.187 (0.0 – 0.5)	1.19 ± 0.441 (0.6 – 1.8)	2.50 ± 1.05 (1.0 – 4.0)	3.43 ± 6.90 (-9.0 – 11.0)
11	2.33 ± 0.263 (2.1 – 2.6)	2.75 ± 1.17 (1.0 – 4.2)	0.10 ± 0.00 (0.10 – 0.10)	0.933 ± 0.423 (0.5 – 1.7)	0.25 ± 1.26 (-1.0 – 2.0)	3.17 ± 2.32 (0.0 – 7.0)

TABLE 4.11. SPATIAL PROFILES OF DI)LVED AND TOTAL METALS (μg/L), SURVEY 2

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	2.31 ± 1.46 (1.5 – 5.6)	4.23 ± 1.67 (2.5 – 7.6)	0.093 ± 0.148 (0.0 – 0.4)	1.64 ± 0.415 (1.2 – 2.2)	0.786 ± 2.16 (-2.0 – 5.0)	6.07 ± 1.92 (3.0 – 9.0)
7	3.14 ± 2.07 (1.3 – 6.7)	4.71 ± 2.18 (2.95 - 8.80)	0.80 ± 0.373 (0.3 – 1.35)	0.533 ± 0.225 (0.3 – 0.9)	20.4 ± 2.87 (16.0 – 23.0)	27.7 ± 3.27 (22.0 – 31.0)
3	1.88 ± 0.343 (1.2 – 2.1)	3.77 ± 0.476 (3.2 – 4.5)	0.167 ± 0.103 (0.1 – 0.3)	1.45 ± 0.493 (1.0 – 2.4)	1.33 ± 3.33 (-3.0 – 7.0)	9.17 ± 1.72 (6.0 – 11.0)
8	2.07 ± 0.632 (1.2 – 3.0)	7.80 ± 2.05 (5.4 – 10.8)	0.343 ± 0.151 (0.2 – 0.6)	2.67 ± 0.582 (2.0 – 3.8)	1.86 ± 1.86 (-1.0 – 5.0)	10.0 ± 1.15 (8.0 – 11.0)
S4	1.74 ± 0.327 (1.2 – 2.25)	4.13 ± 0.575 (3.5 – 5.3)	0.068 ± 0.149 (-0.1 – 0.3)	2.01 ± 0.477 (1.55 – 2.8)	1.63 ± 2.26 (-2.0 – 5.0)	8.63 ± 2.26 (4.0 – 11.0)
B4	1.59 ± 0.543 (1.1 – 2.8)	4.64 ± 0.748 (3.45 – 5.7)	0.1 ± 0.131 (0.0 – 0.4)	2.35 ± 0.878 (1.1 – 3.5)	1.06 ± 1.94 (-1.0 – 4.0)	9.50 ± 1.93 (6.0 – 13.0)
9	9.99 ± 2.18 (6.4 – 12.7)	32.2 ± 15.3 (18.3 – 54.8)	14.7 ± 9.03 (6.5 – 32.7)	14.7 ± 18.5 (0.0 – 50.6)	17.6 ± 4.31 (12.0 – 24.0)	41.6 ± 6.9 (31.0 – 53.0)
5	2.17 ± 0.894 (1.0 – 3.7)	7.51 ± 4.20 (4.0 – 15.3)	1.04 ± 0.439 (0.3 – 1.6)	4.44 ± 1.54 (2.2 – 6.0)	1.71 ± 2.81 (-3.0 – 4.0)	11.4 ± 4.04 (9.0 – 20.0)
10	1.66 ± 0.484 (1.1 – 2.4)	6.28 ± 1.66 (4.3 – 8.8)	0.263 ± 0.288 (0.0 – 0.8)	2.21 ± 1.31 (0.0 – 4.1)	2.5 ± 2.0 (0.0 – 6.0)	8.25 ± 2.55 (5.0 – 13.0)
6	1.24 ± 0.207 (0.9 – 1.6)	4.49 ± 2.71 (1.6 – 10.5)	0.019 ± 0.092 (-0.1 – 0.2)	2.14 ± 1.29 (0.8 – 4.8)	0.00 ± 2.20 (-3.0 – 3.0)	8.75 ± 2.95 (6.0 – 14.0)
11	1.70 ± 0.678 (1.2 – 2.7)	2.73 ± 0.955 (2.1 – 4.4)	0.15 ± 0.058 (0.1 – 0.2)	2.04 ± 1.42 (1.0 – 4.5)	-0.5 ± 1.73 (-2.0 – 2.0)	7.0 ± 1.87 (5.0 – 9.0)

TABLE 4.12. SPATIAL PROFILES OF ISSOLVED AND TOTAL METALS (μg/L), SURVEY 3

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	2.63 ± 0.812 (1.6 – 3.7)	2.99 ± 0.986 (1.9 – 4.2)	0.35 ± 0.278 (0.0 – 0.75)	1.64 ± 0.351 (1.3 – 2.2)	1.7 ± 0.447 (1.0 – 2.0)	5.2 ± 1.3 (3.0 – 6.0)
7	1.16 ± 0.743 (0.6 – 2.2)	7.01 + 4.10 (3.7 - 12.2)	0.15 ± 0.058 (0.1 – 0.2)	1.44 ± 0.095 (1.3 – 1.5)	32.9 ± 2.78 (29.0 – 35.5)	59.0 ± 18.1 (48.0 – 86.0)
3	1.43 ± 0.106 (1.35 – 1.50)	3.08 ± 0.106 (3.0 – 3.15)	0.325 ± 0.177 (0.2 – 0.45)	1.73 ± 0.247 (1.55 – 1.90)	3.25 ± 2.47 (1.5 – 5.0)	8.75 ± 0.354 (8.5 – 9.0)
8	1.94 ± 1.24 (1.0 – 3.7)	9.18 ± 3.32 (6.0 – 14.5)	0.16 ± 0.182 (0.0 – 0.4)	5.42 ± 1.72 (3.5 – 7.6)	3.0 ± 2.45 (0.0 – 6.0)	17.2 ± 2.77 (14.0 – 21.0)
S4	1.0 ± 0.0 (1.0 – 1.0)	2.5 ± 0.0 (2.5 – 2.5)	0.0 ± 0.0 (0.0 – 0.0)	2.9 ± 0.0 (2.9 – 2.9)	2.0 ± 0.0 (2.0 – 2.0)	10.0 ± 0.0 (10.0 – 10.0)
B4	0.9 ± 0.0 (0.9 – 0.9)	3.7 ± 0.0 (3.7 – 3.7)	-0.1 ± 0.0 (-0.1 – -0.1)	3.4 ± 0.0 (3.4 – 3.4)	-2.0 ± 0.0 (-2.0 – -2.0)	12 ± 0.0 (12 – 12)
9	18.5 ± 0.0 (18.5 – 18.5)	39.6 ± 0.0 (39.6 – 39.6)	20.0 ± 0.0 (20.0 – 20.0)	38.9 ± 0.0 (20.0 – 20.0)	25.0 ± 0.0 (25.0 – 25.0)	48.0 ± 0.0 (48.0 – 48.0)
5	1.4 ± 0.0 (1.4 – 1.4)	5.8 ± 0.0 (5.8 – 5.8)	1.0 ± 0.0 (1.0 – 1.0)	3.8 ± 0.0 (3.8 – 3.8)	2.0 ± 0.0 (2.0 – 2.0)	16.0 ± 0.0 (16.0 – 16.0)
10	0.6 ± 0.0 (0.6 – 0.6)	8.3 ± 0.0 (8.3 – 8.3)	0.1 ± 0.0 (0.1 – 0.1)	3.8 ± 0.0 (3.8 – 3.8)	1.0 ± 0.0 (1.0 – 1.0)	12.0 ± 0.0 (12.0 – 12.0)
6	0.8 ± 0.0 (0.8 – 0.8)	3.1 ± 0.0 (3.1 – 3.1)	0.1 ± 0.0 (0.1 – 0.1)	2.9 ± 0.0 (2.9 – 2.9)	2.0 ± 0.0 (2.0 – 2.0)	12.0 ± 0.0 (12.0 – 12.0)
11	2.7 ± 1.79 (1.1 – 4.3)	2.08 ± 1.16 (0.8 – 3.6)	0.1 ± 0.082 (0.0 – 0.2)	2.7 ± 1.51 (1.3 – 4.7)	3.25 ± 1.26 (2.0 – 5.0)	10.8 ± 9.64 (4.0 – 25.0)

TABLE 4.12 (CONT'D)

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
13	1.03 ± 0.153 (0.9 - 1.2)	3.13 ± 1.32 (1.7 - 4.3)	0.233 ± 0.058 (0.2 - 0.3)	1.17 ± 0.153 (1.0 - 1.3)	25.0 ± 3.61 (22.0 - 29.0)	38.7 ± 1.53 (37.0 - 40.0)
14	2.23 ± 0.321 (2.0 - 2.6)	3.83 + 2.58 (2.1 - 6.8)	0.333 ± 0.153 (0.2 - 0.5)	1.73 ± 0.321 (1.5 - 2.1)	8.67 ± 3.21 (5.0 - 11.0)	15.7 ± 6.51 (9.0 - 22.0)
15	2.18 ± 0.077 (2.1 - 2.25)	2.8 ± 0.624 (2.1 - 3.3)	0.367 ± 0.252 (0.1 - 0.6)	1.7 ± 0.1 (1.6 - 1.8)	6.5 ± 1.8 (4.5 - 8.0)	11.5 ± 1.32 (10.5 - 13.0)
16	4.23 ± 3.00 (2.4 - 7.7)	3.27 ± 0.814 (2.7 - 4.2)	0.533 ± 0.551 (0.0 - 1.1)	1.73 ± 0.586 (1.3 - 2.4)	7.33 ± 6.66 (3.0 - 15.0)	13.0 ± 3.0 (10.0 - 16.0)
17	2.7 ± 0.781 (2.2 - 3.6)	4.9 ± 1.92 (3.6 - 7.1)	0.467 ± 0.404 (0.1 - 0.9)	2.3 ± 0.52 (1.7 - 2.6)	4.67 ± 1.53 (3.0 - 6.0)	14.0 ± 1.0 (13.0 - 15.0)
18	2.23 ± 0.058 (2.2 - 2.3)	3.2 ± 1.04 (2.6 - 4.4)	0.467 ± 0.503 (0.0 - 1.0)	2.13 ± 0.416 (1.8 - 2.6)	4.33 ± 2.08 (2.0 - 6.0)	10.0 ± 2.65 (7.0 - 12.0)
19	2.43 ± 0.306 (2.1 - 2.7)	4.33 ± 1.48 (2.7 - 5.6)	0.4 ± 0.3 (0.1 - 0.7)	2.5 ± 0.819 (1.8 - 3.4)	3.33 ± 3.21 (1.0 - 7.0)	6.67 ± 1.53 (5.0 - 8.0)

TABLE 4.13. SPATIAL PROFILES OF DISSOLVED AND TOTAL METALS (μg/L), SURVEY 4

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	1.4	1.3	0.4	2.1	5.0	7.0
7	0.7	2.9	0.2	0.9	35.0	39.0
8	1.5	1.4	0.2	1.8	3.0	5.0
4	1.52 ± 0.318 (1.3 – 1.75)	1.70 ± 0.1 (1.6 – 1.8)	0.15 ± 0.07 (0.1 – 0.2)	1.75 ± 0.07 (1.7 – 1.8)	5.0 ± 0.0 (5.0 – 5.0)	4.75 ± 1.77 (3.5 – 6.0)
11	0.6	4.9	0.2	2.5	1.0	10.0
20	1.4	4.8	0.1	2.8	6.0	15.0
21	1.7	2.6	0.4	1.9	5.0	5.0
22	0.9	3.7	0.2	2.4	3.0	4.0
23	1.75 ± 0.354 (1.5 – 2.0)	4.0 ± 3.11 (1.8 – 6.2)	4.0 ± 0.0 (4.0 – 4.0)	2.75 ± 0.212 (2.6 – 2.9)	4.0 ± 1.41 (3.0 – 5.0)	11.5 ± 7.78 (6.0 – 17.0)
24	0.5	2.7	2.2	2.2	4.0	11.0
25	1.5	2.1	0.4	3.6	7.0	16.0
26	2.4	1.9	0.2	3.1	10.0	15.0
28	2.2	3.4	0.7	2.6	4.0	19.0
29	3.1	8.4	0.5	3.8	11.0	33.0
30	2.4	9.0	0.5	3.8	4.0	15.0

TABLE 4.13 (CONT'D)

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
31	2.2	10.7	0.3	7.9	3.0	28.0
32	2.3	9.7	0.3	4.2	5.0	20.0
33	3.2	5.2	0.3	5.5	5.0	17.0
34	2.5	7.2	0.3	7.4	3.0	24.0
35	2.75	5.35	0.2	3.9	8.0	19.5
36	2.2	3.8	0.3	4.1	19.0	12.0
38	1.75	4.55	0.25	5.25	4.5	14.5

TABLE 4.14. SPATIAL PROFILES OF DISSOLVED AND TOTAL METALS (μg/L), SURVEY 5

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	1.7	2.5	0.1	1.55	2.5	-1.5
7	0.9	2.0	0.4	0.6	32.0	32.0
8	1.2	11.3	0.1	8.3	4.0	19.0
4	1.3	6.4	0.2	4.1	7.0	11.0
11	1.6	3.2	0.2	3.1	6.0	8.0
25	1.4	3.3	0.2	0.2	5.0	2.0
26	2.3	5.5	0.2	4.3	6.0	12.0
29	3.5	10.9	0.5	4.8	3.0	21.0
41	3.2	12.1	0.4	7.3	5.0	15.0
42	3.2	9.1	0.3	3.7	-1.0	18.0
43	2.5	7.8	0.3	14.4	12.0	9.0
44	2.7	6.8	0.3	4.2	1.0	9.0
45	2.3	5.3	0.2	3.8	2.0	12.0
46	2.1	4.7	0.4	4.1	8.0	3.0
47	2.2	5.6	0.25	5.1	5.5	18.5

TABLE 4.15. SPATIAL PROFILES OF DISSOLVED AND TOTAL METALS (μg/L), SURVEY 6

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	2.8	8.9	0.1	7.1	5.0	21.0
4	2.7	9.4	0.1	7.4	5.0	19.0
26	2.6	7.25	0.65	5.7	2.5	22.0
29	5.4	13.6	0.3	6.2	4.0	20.0

TABLE 4.16. SPATIAL PROFILES OF DISSOLVED AND TOTAL METALS (μg/L), SURVEY 7

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	2.1	5.8	0.1	3.8	2.0	11.0
4	2.0	5.2	0.1	1.8	0.0	1.0
26	2.0	8.2	0.1	3.8	2.0	10.0
29	4.7	14.1	0.2	3.0	-1.0	9.0

TABLE 4.17. SPATIAL PROFILES OF DISSOLVED AND TOTAL METALS (μg/L), SURVEY 8

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	1.8	4.7	0.1	1.5	4.0	6.0
4	2.1	6.05	0.15	1.55	5.5	8.0
26	1.6	4.6	0.1	1.1	0.0	10.0
29	3.8	9.8	0.1	1.3	-1.0	6.0

TABLE 4.18. SPATIAL PROFILES OF DISSOLVED AND TOTAL METALS (μg/L), SURVEY 9

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	1.6	3.1	0.7	1.0	0.0	6.0
4	0.3	2.8	1.0	5.0	1.0	9.0
26	1.3	2.7	0.0	1.0	0.0	6.0
29	2.9	10.8	0.2	1.9	2.0	11.0

TABLE 4.19. SPATIAL PROFILES OF DISSOLVED AND TOTAL METALS (μg/L), SURVEY 10

STATION	COPPER		CHROMIUM		ZINC	
	DISSOLVED	TOTAL	DISSOLVED	TOTAL	DISSOLVED	TOTAL
1	1.85	3.85	0.15	0.55	4.0	15.0
4	1.1	4.3	0.0	1.9	0.0	9.0
26	1.3	1.9	0.1	0.5	3.0	2.0
29	2.8	9.5	0.3	1.9	-1.0	4.0

TABLE 4.20. SUMMARY OF DATA FROM SELECTED STATIONS FOR 10 SURVEYS OF MONROE HARBOR (1983-1984).

SURVEY	TOTAL PCBs, ng/L			TOTAL CHROMIUM, µg/L			TOTAL COPPER, µg/L			TOTAL ZINC, µg/L		
	STA. 1	STA. 4	STA. 6	STA. 1	STA. 4	STA. 6 (26)*	STA. 1	STA. 4	STA. 6 (26)*	STA. 1	STA. 4	STA. 6 (26)*
1	9.3	51	14	1.6	2.0	1.2	3.9	4.0	3.3	4.1	4.4	3.4
2	10	388	32	1.6	2.0	2.1	4.2	4.1	4.5	6.1	8.6	8.8
3	11	220	17	1.6	2.9	2.9	3.0	2.5	3.1	5.2	10.0	12
4	12	16	8	2.1	1.8	3.1	1.3	1.7	1.9	7.0	4.8	15
5	5.9	110	-	1.6	4.1	4.3	2.5	6.4	5.5	-1.5	11	12
6	13	14	-	7.1	7.4	5.7	8.9	9.4	7.3	21	19	22
7	8.4	6.7	-	3.8	1.8	3.8	5.8	5.2	8.2	11	1	10
8	6.9	85	-	1.5	1.6	1.1	4.7	6.1	4.6	6	8	10
9	4.9	93	-	1.0	5.0	1.0	3.1	2.8	2.7	6	9	6
10	4.5	210	-	0.6	1.9	0.5	3.9	4.3	1.9	15	9	2
TOTALS	8.6±3.0 (4.5-13)	119±121 (6.7-388)	18±10 (8-32)	2.3±1.9 (0.6-7.1)	3.1±1.9 (1.6-7.4)	2.6±1.7 (0.5-5.7)	4.1±2.1 (1.3-8.9)	4.7±2.3 (1.7-9.4)	4.5±2.3 (1.9-8.2)	8.3±5.8 (-1.5-21)	8.5±4.8 (1-19)	10.1±5.8 (2-22)

*For metals data, Sta. 6 used in Surveys 1-3; Sta. 26 in Surveys 4-10.